THE ROYAL SOCIETY.

30th November, 1895.
THE ROYAL SOCIETY. Nov. 30, 1895.

Her Sacred Majesty QUEEN VICTORIA, Patron.

Date of Election.
1863, Feb. 12.  HIS ROYAL HIGHNESS THE PRINCE OF WALES, K.G.
1882, Mar. 16.  HIS ROYAL HIGHNESS THE DUKE OF EDINBURGH, K.G.
1893, June 8.  HIS ROYAL HIGHNESS THE DUKE OF YORK, K.G.
THE COUNCIL
OF
THE ROYAL SOCIETY.

SIR JOSEPH LISTER, Bart., F.R.C.S., D.C.L.—President.
PROF. MICHAEL FOSTER, M.A., M.D.—Secretary.
THE LORD RAYLEIGH, M.A., D.C.L.—Secretary.
EDWARD FRANKLAND, D.C.L., LL.D.—Foreign Secretary.
WILLIAM CROOKES, F.R.S.—Vice-President.
SIR JOSEPH FAYRER, K.C.S.I.
LAZARUS FLETCHER, M.A.
WALTER HOLBROOK GASKELL, M.D.
WILLIAM HUGGINS, D.C.L.—Vice-President.
THE LORD KELVIN, D.C.L.

PROF. ALEXANDER B. W. KENNEDY, LL.D.
PROF. HORACE LAMB, M.A.
PROF. EDWIN RAY LANKESTER, M.A.—Vice-President.
PROF. CHARLES LAPWORTH, LL.D.
MAJOR PERCY ALEXANDER MACMAHON, R.A.
PROF. JOHN HENRY POYNTING, D.Sc.
PROF. ARTHUR WILLIAM RUCKER, M.A.
OSBERT SALVIN, M.A.
PROF. HARRY MARSHALL WARD, D.Sc.
ADM. WILLIAM JAMES LLOYD WHARTON, C.B.

* * This Council will continue till November 30, 1896.

Assistant-Secretary and Librarian.
HERBERT RIX, R.A.

Clerk.
THEODORE E. JAMES.

Assistant Librarian.
A. HASTINGS WHITE.

Office and Library Assistant.
RICHARD CHAPMAN.

Omissions having occasionally occurred in the Annual List of Deceased Fellows, as announced from the Chair at the Anniversary Meeting of the Royal Society, it is requested that any information on that subject, as also Notice of Changes of Residence, be addressed to the Assistant Secretary.
<table>
<thead>
<tr>
<th>Date of Election</th>
<th>Served on Council</th>
<th>Committee</th>
<th>Name and Qualifications</th>
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<tbody>
<tr>
<td>June 1, 1876</td>
<td>1873–75</td>
<td>Rm.</td>
<td>Abney, William de Wivelisec, Capt. R.E. C.B. D.C.L. (Dunelm.) F.I.C. F.C.S. F.R.A.S., Director for Science in the Science and Art Department. Rathmore Lodge, Bolton-gardens South, Earl's Court, S.W.; and Athenaeum Club. S.W.</td>
</tr>
<tr>
<td>June 6, 1889</td>
<td></td>
<td>*</td>
<td>Aitken, John, F.R.S.E. D.D. Dalroch, Falkirk. N.B.</td>
</tr>
<tr>
<td>June 12, 1884</td>
<td></td>
<td>*</td>
<td>Allman, George Johnston, LL.D. (Dubl.) D.Sc. Emeritus Professor of Mathematics in Queen's College, Galway, Member of Senate of the Royal University of Ireland. St. Mary's, Galway.</td>
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<td>Date of Election</td>
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<td>June 12, 1884</td>
<td>1892-1894</td>
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**FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)**


Archer, William, M.R.I.A. *National Library of Ireland; and 52 Lower Mount-street, Dublin.*


† Armstrong, Henry Edward, Ph.D. (Lips.) LL.D. (St. Andr.) Pres. Chem. Soc. Professor of Chemistry at the City and Guilds of London Central Institute, South Kensington, Hon. Mem. Pharm. Soc. Lond. 55 Granville-park, Lewisham. S.E.


* Baird, Andrew Wilson, Lieut.-Colonel, R.E. Care of Messrs. Grindlay, Groom & Co., Bombay, India.*


† Balfour, Right Hon. Arthur James, D.C.L. 4 Carlton-gardens, S.W.; and Whittinghame, Prestonkirk, N.B.

FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)


* Ballard, Edward, M.D. 6 Ravenscroft-park, High Barnet, Herts.

† Barkly, Sir Henry. G.C.M.G. K.C.B. F.R.G.S. 1 Bina-gardens, South Kensington, S.W.


Barrow, John, F.S.A., F.R.G.S. 17 Hanover-terrace, Regent's Park. N.W.


* Basset, Alfred Barnard, M.A. Fledborough Hall, Holtpoort, Berks.


† Bateman, James, M.A. F.L.S. Home House, Worthing.


* Beddard, Frank Evers, M.A. (Oxon.), F.R.S.E., F.Z.S., Lecturer on Comparative Anatomy, Guy's Hospital, Prosector to the Zoological Society. Zoological Society's Gardens, Regent's Park. N.W.


* Bell, James, C.B. D.Sc. (Dubl.) Ph.D. F.I.C. Late Principal of the Inland Revenue Laboratory, Somerset House. Howell Hill Lodge, Ewell, Surrey.


* Bidwell. Shelford. M.A. LL.B. Riverstone Lodge, Southfields, Wondsworth S.W.

Blake, Henry Wollaston, M.A. 8 Devonshire-place, Portland place. W.

### Fellows of the Society. (Nov. 30, 1895.)

<table>
<thead>
<tr>
<th>Date of Election</th>
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<td>June 5, 1890.</td>
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<td>June 11, 1857</td>
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<td>June 4, 1885</td>
<td>1885-95</td>
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</table>


* Burbury, Samuel Hawksley, M.A. 17 Upper Phillimore-gardens, Kensington, W.

* Burnside, William, M.A. Professor of Mathematics, Royal Naval College, Greenwich. *The Laurels, Hithergreen-lane, S.E.*

* Callendar, Hugh Longbourne, M.A. Late Fellow of Trinity College, Cambridge, Professor of Physics in McGill College, Montreal. *McGill College, Montreal, Canada.*

† Carruthers, William, V.P.L.S. F.G.S. Keeper of the Botanical Department, British Museum. *Central House, Central-hill, S.E.; and British Museum (Nat. Hist.), Cromwell-road, S.W.*

* Cash, John Theodore, M.D. Regius Professor of Materia Medica in the University of Aberdeen. 25 Dees-street, Aberdeen.*

† Chamberlain, Right Hon. Joseph, LL.D. (Cantab.). 40 Prince's-gardens; and *Atheneum Club, S.W.*

Chambers, Charles, Director of the Colaba Observatory, Bombay. *Colaba Observatory, Bombay.*

* Cheyne, William Watson, M.B. C.M. (Edin.) F.R.C.S. (Eng.) Professor of Surgery in King's College, London. 75 Harley-street, W.*

† Childers, Right Hon. Hugh Culling Eardley, F.R.G.S. 6 St. George's-place, S.W.; *Brooks's and Athenaeum Clubs, S.W.*


* Church, Arthur Herbert, M.A. (Oxon.) F.C.S. F.I.C. Professor of Chemistry in the Royal Academy of Arts, Lecturer on Organic Chemistry, Royal Indian Engineering College, Cooper's Hill. *Shelsley, Kid.*

* Clark, Latimer, Mem. Inst. C.E. F.R.A.S. 11 Victoria-street, S.W.*


* Clarke, Charles Baron, M.A. (Cantab.) F.L.S. F.G.S. 13 Kew Gardens-road, Kew.*

Cicland, John, M.D. D.Sc. LL.D. Professor of Anatomy in the University of Glasgow. *University, Glasgow.*

† Clerk, Henry, Major-General, R.A. 40 St. Ermin's Mansions, Caxton-street, Westminster, S.W.


* Common, Andrew Ainslie, Treas. R.A.S. LL.D. (St. And.) D.Sc. 63 Eaton-rise, Laling, W.*
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**FELLOWS OF THE SOCIETY. (Nov. 30, 1895)**

* Conroy, Sir John, Bart., M.A. F.C.S. Fellow and Bedford Lecturer of Balliol College, Oxford. **Balliol College, Oxford.**

† Cotterill, James Henry, M.A. Professor of Applied Mechanics, Royal Naval College, Greenwich. **18 Gloucester-place, Greenwich. S.E.**


† Crofton, Morgan William, D.Sc. Fellow of the Royal University of Ireland 15 Ambrose-place, Worthing.


* Cunningham, Daniel John, M.D. (Edin. and Dubl.), D.Sc. D.C.L. LL.D. Prof. of Anatomy in the University of Dublin. **43 Fitzwilliam-place, Dublin.**

Cunningham, David Douglas, M.B. C.M. (Edin.) C.I.E. F.I.S. Brigade Surg. Lieut.-Col. Bengal Medical Service. Honorary Surgeon to the Viceroy of India. Professor of Physiology in the Medical College, and Fellow of the University of Calcutta. **9 Loudon-street, Calcutta.**


† Davey, Right Hon. Horace, Lord, M.A. D.C.L. **36 Brook-street, W.; and Verdley-place, Fernhurst, Sussex.**


* Dawson, George Mercer, C.M.G. LL.D. F.G.S. A.R.S.M. F.R.S.C. Assistant Director of the Geological Survey of Canada. **Sussex-street, Ottawa, Canada.**

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<th>Date of Election</th>
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<th>Date</th>
<th>Name and Address</th>
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<tr>
<td>June 6, 1861</td>
<td></td>
<td>'70-'72</td>
<td>Debus, Heinrich, Ph.D. F.C.S. Late Prof. of Chemistry at the Royal Naval College, Greenwich, Lecturer on Chemistry at Guy’s Hospital. 4 Schlangenweg, Cassel, Hessen, Germany.</td>
</tr>
<tr>
<td>June 7, 1877</td>
<td>85–86</td>
<td>Ru.</td>
<td>Dewar, James, M.A. F.C.S. F.R.S.E. Hon. LL.D. (Glas. and St. And.) Jacksonian Prof. of Natural Experimental Philosophy in the University of Cambridge, Fullerman Prof. of Chemistry in the Royal Institution. 1 Scropo-terrace, Cambridge; and Royal Institution, Albemarle-street. W.</td>
</tr>
<tr>
<td>June 4, 1885</td>
<td></td>
<td></td>
<td>Divers, Edward, M.D. Professor of Chemistry in the Imperial University, Japan. Hongo, Tokyo, Japan.</td>
</tr>
<tr>
<td>June 4, 1886</td>
<td></td>
<td></td>
<td>* Dixon, Harold B., M.A. F.C.S. Prof. of Chemistry and Director of the Chemical Laboratories in Owens College, Manchester. Birch Hall, Rusholme, Manchester.</td>
</tr>
<tr>
<td>June 1, 1876</td>
<td>79–81</td>
<td></td>
<td>* Dunkin, Edwin, F.R.A.S. Formerly Chief Assistant, Royal Observatory, Greenwich. Kenwyn, Kidbrooke Park-road, Blackheath. S.E.</td>
</tr>
<tr>
<td>June 1, 1893</td>
<td></td>
<td></td>
<td>Dunstan, Wyndham R., M.A. (Oxon.) Sec. Chem. Soc. F.I.C. Professor of Chemistry to, and Director of the Research Laboratory of, the Pharmaceutical Society of Great Britain. Lecturer on Chemistry at St. Thomas’s Hospital. 3 Percy-villas, Campden Hill, Kensington. W.</td>
</tr>
<tr>
<td>June 3, 1875</td>
<td></td>
<td></td>
<td>Dupré. August, Ph.D. F.C.S. Lecturer on Chemistry at the Westminster Hospital. Westminster Hospital Medical School, Caxton-street, Westminster, S.W.; and Cliftonville, Sutton, Surrey.</td>
</tr>
<tr>
<td>June 12, 1873</td>
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<td>* Ellery, Robert Lewis John, C.M.G. F.R.A.S. Late Government Astronomer, and Director of the Observatory. Melbourne, Victoria.</td>
</tr>
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FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)


Erichsen, Sir John Eric, Bart., F.R.C.S. LL.D. (Edin.) Surgeon Extraordinary to the Queen, Pres. of and Emeritus Prof. of Surgery to University College, and Consulting Surgeon to the Hospital. 6 Cavendish-place, Cavendish-square, W.


* Everett, Joseph David, M.A. D.C.L. F.R.S.E. Professor of Natural Philosophy in Queen's College, Belfast. Derrycyle Aveue, Belfast.

* Ewart, James Cossar, M.D. Professor of Natural History in the University of Edinburgh. The University, Edinburgh.


† Fayrer, Sir Joseph, K.C.S.I. M.D. (Edin. and St. And.) F.R.C.P. (Lond.) F.R.C.S. F.R.S.E. Honorary Physician to the Queen. 16 Devonshire-street, Portland-place. W.


Ferrier, David, M.A. (Aberd.) M.D. (Edin.) LL.D. F.R.C.P. Professor of Neuro-pathology, King's College, London. 34 Cavendish-square. W.

* Festing, Edward Robert, Major-General, R.E. (retired). Science Museum Director, South Kensington Museum. South Kensington. S.W.

* Fitzgerald, Prof. George Francis, M.A. D.Sc. 40 Trinity College, Dublin.

* Fleming, John Ambrose, M.A. (Camb.) D.Sc. (Lond.) Late Fellow of St. John's College, Cambridge, Fellow and Professor of Electrical Engineering in University College, London. University College, Gover-street. W.C.
FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)

Date of Election. Served on Council.

June 6, 1889.


June 9, 1887.


June 2, 1892.

Foster, George Carey, B.A. F.C.S. Professor of Physics in University College, London. 18 Daleham-gardens, South Hampstead, N.W.; and Athenæum Club. S.W.


† Fraser, Thomas Richard, M.D. (Edin.) F.R.C.P. & R.S. (Edin.) LL.D. (Aberdeen) Professor of Materia Medica and Clinical Medicine in the University, Edinburgh. 13 Drumshagne-gardens, Edinburgh.


* Gairdner, William Tennant, M.D. (Edin.) Hon. M.D. (Dubl.) LL.D. (Edin.) F.R.C.P. (Edin.) Hon. F.R.C.P. (Irel.) Professor of Medicine in the University of Glasgow. Physician in Ordinary to the Queen in Scotland. The University, Glasgow.


† Gamgee, Arthur, M.D. M.R.C.P. (Lond.) & F.R.C.P. (Edin.) 8 Avenue de la Gare, Lausanne, Switzerland.


† Garrod, Sir Alfred Baring, M.D. Coll. Reg. Med. Socie. Physician Extraordinary to the Queen, Consulting Physician to King’s College Hospital. 10 Harley-street. W.

† Gaskell, Walter Holbrook, M.A. M.D. (Camb.) LL.D. (Edin.) Lecturer in Physiology at Cambridge. The Uplands, Great Shelford, near Cambridge.

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<td>Feb. 3, 1881</td>
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Giffen, Sir Robert, K.C.B. LL.D. (Glasc.) 44 Pembroke-road, Kensington. W.


Gilchrist, Percy Carlyle, A.R.S.M. Fugnat Bank, Finchley-road, Hampstead. N.W.


Gladstone, John Hall, Ph.D. Sc.D. (Dubl.) V.P.C.S. 17 Pembroke-square. W.

† Gladstone, Right Hon. William Ewart, D.C.L. Hawarden, Chester.

Glaisher, James, F.R.A.S. Ord. Bras. Rosae Eq. The Skota, Heathfield Road, South Croydon.


Godman, Frederick Ducane, F.L.S. F.G.S. F.E.S. 10 Chandos-street, Cavendish-square, W.; and South Lodge, Horsham.


Goschen, Right Hon. George Joachim, M.A. 69 Portland-place. W.


* Gowers, William Richard, M.D. F.R.C.P. Fellow of University College, London, Consulting Physician to University College Hospital. Physician to the National Hospital for the Paralysed and Epileptic. 50 Queen Anne-street. W.

† Grant Duff, Right Hon. Sir Mountstuart Elphinstone, G.C.S.I. V.-P.R.G.S. Athenæum Club; and York House, Twickenham.
FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)


* Greenhill, Alfred George, M.A. Professor of Mathematics in the Artillery College, Woolwich. 10 New Inn, W.C.


* Griffiths, Ernest Howard, M.A. 12 Parksides, Cambridge.


* Groves, Charles Edward, F.C.S. F.I.C. 352 Kennington-road, S.E.


* Halliburton, William Dobinson, M.D. B.Sc. Professor of Physiology in King’s College, London. 9 Ridgmount-gardens, Gower-street, W.C.

† Halsbury, Right Hon. Hardingie Stanley Giffard, Lord, M.A. D.C.L. 4 Ennismore-gardens, W.


* Hartley, Walter Noel, F.R.S.E. F.I.C. Professor of Chemistry in the Royal College of Science for Ireland. Royal College of Science, Stephen’s-green, Dublin; and 36 Waterloo-road, Dublin.


FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)

† Hayward, Robert Baldwin, M.A.  
Ashcombe, Shanklin, Isle of Wight.

Paiington, Devon.

Hector, Sir James, K.C.M.G. Ord. Cr. Pruss. M.D. F.G.S. F.L.S. F.R.S.E.  
C.M.Z.S., Hon. Mem. of the Royal Societies of Victoria, New South Wales,  
Mining Engrs., and K. Leop. Carol. Acad.; Director of the Geological  
Survey, Colonial Laboratory, Meteorological and Weather Departments,  
and of the New Zealand Institute; Chancellor of the New Zealand  
University. Wellington, New Zealand.

Assistant in the Herbarium, Royal Gardens, Kew.  
Herbarium, Royal Gardens, Kew.

Deputy Surveyor-General in charge of the Trigonometrical Surveys,  
Survey of India. Merrivale, 18 Allée-park, West Dulwich, S.E.; and  
Atheneum Club. S.W.

Hennessey, Henry G., M.R.I.A. Professor of Applied Mathematics and Mechanism  
in the Roy. Coll. of Science for Ireland. Clarens, Montreux, Switzerland.

† Henrici, Olaus Magnus Friedrich Erdmann, Ph.D. LL.D. (St. And.) Professor of  
Mechanics and Mathematics in the City and Guilds of London Institute.  
Central Technical College, Exhibition-road, S.W.; and 34 Clarendon-road,  
Nottingham. W.

* Herdmann, William Abbott, D.Sc. F.R.S.E. F.L.S. Professor of Natural History  
in University College, Liverpool. University College, Liverpool.

Professor of Physics and Experimental Philosophy in the Durham  
College of Science, Newcastle-on-Tyne. Observatory House, Slough,  
Bucks.

† Herschel, John, Col. R.E. F.R.A.S. Late Deputy Superintendent, Great  
Trigonometrical Survey of India. Observatory House, Slough, Bucks.

† Herschell, Right Hon. Farrer, Lord, G.C.B. D.C.L. LL.D. Chancellor of the  
University of London. 46 Grosvenor-gardens. S.W.

Heycock, Charles Thomas, M.A.  
Lecturer on Natural Science, King's College,  

Heywood, James, M.A. F.G.S. F.S.A. 26 Kensington Palace-gardens, W.; and  
Atheneum Club. S.W.

Geol. Soc. Liverpool. Hendon-poque, Hendon. N.W.

† Hicks, John Braxton, M.D. (Lond.) F.L.S. Coll. Reg. Med. Soc. The Brackens,  
Lymington, Hants.

* Hicks, William Mitchinson, M.A. D.Sc. Late Fellow of St. John's College,  
Cambridge. Principal and Professor of Physics in Firth College, Sheffield.  
Dunheved, Endcliffe-crescent, Sheffield.

* Hickson, Sidney John, D.Sc. (Lond.) M.A. (Camb.) Hon. M.A. (Oxon.) F.L.S.  
Fellow of Downing College, Cambridge; Professor of Zoology in Owens  
College, Manchester. Ellesmere House, Wilmslow Road, Fallowfield, Man-  
chester.
FELLOWS OF THE SOCIETY. (Nov. 30, 1895)

† Hincks, Rev. Thomas, B.A. (Lond.) Stokeleigh, Leigh Woods, Clifton, Bristol.
† Hippisley, John, F.R.A.S. Atheneum Club, S.W.; and Stoneaston Park, Bath.
* Horsley, Victor Alexander Haden, B.S. P.R.C.S. M.D. (Halle) Professor of Pathology in University College, London. 25 Cavendish-square, W.; and Atheneum Club. S.W.
* Hudleston, Wilfrid H., M.A. F.G.S. F.C.S. 8 Stanhope-gardens, South Kensington. S.W.
FELLOWS OF THE SOCIETY. (Nov. 30, 1893.)


Jackson, Right Hon. William Lawies. 27 Cadogan-square, S.W.; and Allerton Hall, Chapel Allerton, Leeds.

* Japp, Francis Robert, M.A. Ph.D. LL.D. (St. And.) F.I.C. F.C.S. Prof. of Chemistry in the University of Aberdeen. University, Aberdeen.


* Jones, John Viriamu, M.A. (Oxon.) B.Sc. (Lond.) Principal and Professor of Physics in the University College of South Wales and Monmouthshire, Fellow of University College, London. 42 Park-place, Cardiff.

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<th>Name</th>
<th>Title and Institution</th>
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<tr>
<td>June 5, 1890</td>
<td></td>
<td>* Kerr, Rev. John, LL.D.</td>
<td>Mathematical Lecturer in the Free Church Training College, Glasg. 113 Hill-street, Glasg.</td>
</tr>
<tr>
<td>June 3, 1875</td>
<td>1878–90</td>
<td>† Klein, Edward Emanuel, M.D.</td>
<td>Lecturer on General Anatomy and Physiology in the Medical School, St. Bartholomew's Hospital. 19 Earl's Court-square. S.W.</td>
</tr>
<tr>
<td>June 12, 1884</td>
<td>1894–95</td>
<td>* Lamb, Horace, M.A. ( Cantab.)</td>
<td>Professor of Mathematics in the Owens College, Manchester. Burton-road, Didsbury, Manchester.</td>
</tr>
<tr>
<td>June 7, 1883</td>
<td>R.</td>
<td>* Langley, John Newport, M.A.</td>
<td>Fellow and Lecturer of Trinity College, Lecturer on Histology in the University of Cambridge. Trinity College, Cambridge.</td>
</tr>
<tr>
<td>June 2, 1892</td>
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<td>Larmor, Joseph, M.A. D.Sc. (Lond.)</td>
<td>Fellow of St. John's College, Cambridge; late Professor of Natural Philosophy in Queen's College, Galway, and Fellow of the Royal University of Ireland. St. John's College, Cambridge.</td>
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FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)

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<td>June 9, 1887</td>
<td>* Lodge, Oliver Joseph, D.Sc. LL.D. (St. And.) Professor at Physics in University College, Liverpool. 2 Grove-park, Liverpool.</td>
</tr>
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**FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)**

*Lydekker, Richard, B.A. (Camb.), The Lodge, Harpenden, Herts.*

*Maclester, Alexander, M.A. M.D. (Dubl. & Camb.) M.D. Sc.D. (Dubl.) LL.D. (Glasg.) Professor of Anatomy in the University of Cambridge. Torrisdale, Cambridge.*


*McIntosh, Sir Francis Leopold, Admiral, K.C.B. D.C.L. LL.D. 8 Atherstone-terrace, Gloucester-road. S.W.*

*McCoy, Sir Frederick, K.C.M.G. M.A. D.Sc. (Cantab.) F.G.S. Professor of Natural Sciences in the University, Melbourne, Soc. Phil. Cantab. Soc. Honor. Melbourne, Australia.*

†Macdonald, John Denis, M.D. Inspector-General of Hospitals and Fleets, R.N. 82 Messina-avenue, West Hampstead. N.W.


*Maeeven, William, M.D. (Glasg.) Hon. LL.D. (Glasg.) Professor of Surgery in the University of Glasgow. 3 Woodside-crescent, Glasgow.*

*McKendrick, John Gray, M.D. LL.D. F.R.S.E. F.R.C.P.E. Professor of Physiology in the University of Glasgow. 2 Florentine-gardens, Glasgow.*


*McLeod, Herbert, F.I.C. F.C.S. Professor of Chemistry in the Royal Indian Engineering College, Cooper's Hill. The College, Cooper's-hill, Staines.*


**FELLOWS OF THE SOCIETY.** (Nov. 30, 1895)

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<tr>
<td><em>Martin, Henry Newell, M.A. (Camb.) M.B. and D.Sc. (Lonld.) (Hon.) M.D. Univ. of Georgia.</em></td>
<td>Physiological Laboratory, University, Cambridge.</td>
</tr>
<tr>
<td><em>Martin, Sidney, M.D. B.S. B.Sc. F.R.C.P.</em></td>
<td>Assistant Physician in University College Hospital, and in the Hospital for Consumption, Brompton. 10 Mansfield-street, Cavenish-square, W.</td>
</tr>
<tr>
<td><em>Matthey, George, F.C.S. Assoc. Inst. C.E. Leg. Honor. (France), Ord. Franz Josef (Austria), Great Gold Medal for Arts and Science (Germany).</em></td>
<td>Chyne House, Chelsea Embankment. S.W.</td>
</tr>
<tr>
<td><em>Medlicott, Henry Benedict, M.A. (Dubl.) F.G.S.</em></td>
<td>Late Director (1876-57) of the Geol. Survey of India. 43 St. John's-road, Clifton, Bristol.</td>
</tr>
<tr>
<td><em>Meldola, Raphael, For. Sec. C.S. F.I.C. F.R.A.S. F.E.S.</em></td>
<td>Professor of Chemistry in the Finsbury Technical College, City and Guilds of London Institute. 6 Brunswick-square, W.C.</td>
</tr>
<tr>
<td>Mills, Edmund James, D.Sc. F.C.S. F.I.C. Young Professor of Technical Chemistry in the Glasgow and West of Scotland Technical College, Glasgow. 60 John-street, Glasgow.</td>
<td></td>
</tr>
<tr>
<td>Milne, John, F.G.S. Assoc. and Hon. Fellow of King's College, London, Late Professor of Mining and Geology in the Imperial College of Engineering, Japan. Shide Hill House, Shide, Newport, Isle of Wight.</td>
<td></td>
</tr>
<tr>
<td><em>Minchin, George M., M.A. (Dubl.).</em></td>
<td>Professor of Mathematics in the Royal Indian Engineering College, Cooper's-hill. The College, Cooper's-hill, Staines.</td>
</tr>
<tr>
<td>Moore, John Carrick, M.A. F.G.S. 113 Eaton-square, S.W.; and Corwall, Stannarae, Wigtownshire.</td>
<td></td>
</tr>
<tr>
<td><em>Morley, Right Hon. John, M.A. (Oxon.) Hon. LL.D. (Camb. and Glasg.)</em></td>
<td>95 Elm Park Gardens; and Athenæum Club. S.W.</td>
</tr>
<tr>
<td><em>Moulton, John Fletcher, M.A. Q.C.</em></td>
<td>57 Oneley-square. S.W.</td>
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### Fellows of the Society (Nov. 30, 1895)

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<th>Date of Election</th>
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<tr>
<td>Müller, Hugo, Ph.D., LL.D. (St. And.) V.P.C.S. Ord. Ss^ruum^ Lazar. et Maur. Eq. 13 Park-square, N.W.; Crosby-hill, Camberley, Surrey; and Athenaum Club. S.W.</td>
<td>June 7, 1866.</td>
<td></td>
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<tr>
<td>Mundella, Right Hon. Anthony John. 16 Eleavton-place; and Athenæum and Reform Clubs. S.W.</td>
<td>June 3, 1875.</td>
<td></td>
</tr>
<tr>
<td>† Nares, Sir George Strong, Vice-Admiral, K.C.B. 1 Beaufort-villas, Surbiton.</td>
<td>June 2, 1870.</td>
<td></td>
</tr>
<tr>
<td>Niven, Charles, M.A., F.R.A.S., Professor of Natural Philosophy in the University, Aberdeen. 6 Charnoney, Old Aberdeen.</td>
<td>June 8, 1882.</td>
<td></td>
</tr>
<tr>
<td>† Northbrook, Thomas George Baring, Earl of, LL.D., D.C.L., G.C.S.I. 4 Hamilton-place, W.; and Stratton, Micheledtree Station, Hants.</td>
<td>June 5, 1890.</td>
<td></td>
</tr>
<tr>
<td>† Paget, Sir James, Bart., D.C.L. (Oxon.) LL.D. (Cantab. et Edin.) Hon. M.D. (Dubl.) Corr. Mem. Inst. Fr. (Aed. Sei.) Late Vice-Chancellor of the University of London, Surjeant-Surgeon to the Queen, Surgeon in Ordinary to H.R.H. the Prince of Wales. 5 Park-square West, Regent's Park. N.W.</td>
<td>June 5, 1851.</td>
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</table>
FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)


† Parsons, R. Mann. Major-General R.E. Hyde-vale, Blackheath. S.E.

† Pavy, Frederick William, M.D. (Lond.), LL.D. (Glas.) Coll. Reg. Med. Socius, Consulting Physician and formerly Lecturer on Physiology and Comparative Anatomy and Zoology, and on Medicine, at Guy's Hospital. 35 Grosvenor-street. W.


Pedler, Alexander, F.C.S. F.I.C Fellow of the University of Calcutta; Professor of Chemistry, Presidency College, Calcutta; and Meteorological Reporter to the Government of Bengal. Presidency College, Calcutta.


Perkin, William Henry, V.P.C.S. LL.D. (St. And.) Ph.D. The Chestnuts, Sullbury, Harrow.


* Perry, John, D.Sc. Professor of Mechanical Engineering and Applied Mathematics in the City and Guilds of London Technical College, Finsbury. 31 Brunswick-square. W.C.

Pettigrew, James Bell, M.D. and F.R.C.P. (Edin.), LL.D. (Glasg.) Professor of Medicine and Anatomy and Dean of the Medical Faculty in the University of St. Andrews; Laureate Inst. Fr. St. Andrews. N.B.


† Pirbright, Right Hon. Baron Henry de Worms, Lord. 42 Grosvenor-place, S.W.; Hanley-park, Guildford.


* Poulton, Edward Bagnall, M.A. (Oxon.) F.L.S. F.Z.S. F.G.S. Hope Professor of Zoology in the University of Oxford. Wykeham House, Banbury-road, Oxford; and St. Helen's Cottage, St. Helen's, Isle of Wight.

* Power, William Henry, Assistant Medical Officer, Local Government Board, Glenbrook, Greenhithe; and Local Government Board, Whitehall. S.W.

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* Purdie, Thomas, B.Sc. Ph.D. A.R.S.M. Professor of Chemistry in the University of St. Andrews. The University, St. Andrews.

Pye-Smith, Philip Henry, M.D. B.A. F.R.C.P. Physician to Guy's Hospital, late Lect. on Physiol. at Guy's Hospital. 48 Brook-street. W.

Quain, Sir Richard, Bart., M.D. (Lond.) Hon. M.D. (Dubl. and Roy. Univ. Irel.) Hon. LL.D. (Edin.) F.R.C.P. Hon. F.R.C.P. Irel. President of the General Medical Council, Physician Extraordinary to the Queen, Fellow of the University of London. 67 Harley-street, W.; and Athenaeum and Union Clubs. S.W.


† Reed, Sir Edward James, K.C.B. Broadway-chambers, Westminster. S.W.

* Reinoeld, Arnold William, M.A. Professor of Physics in the Royal Naval College, Greenwich. 28 Belhaven Hill, Lee. S.E.


<table>
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<th>Date of Election</th>
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<td>June 4, 1885</td>
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<td>* Ringer, Sydney, M.D. (Lond.) Holme Professor of Clinical Medicine, University College, London. 15 Cavel-indexplace. W.</td>
</tr>
<tr>
<td>June 6, 1878</td>
<td></td>
<td>† Roberts, Samuel, M.A. (Lond.). 34 Lady Margaret-road, St. John's College Park. N.W.</td>
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<tr>
<td>June 12, 1884</td>
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<td>* Roy, Charles Smart, M.D. (Edin.) Professor of Pathology in the University of Cambridge. Trinity College, Cambridge.</td>
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FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)

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† Russell, William James, Ph.D. V.P.C.S. Lecturer on Chemistry at the Medical School of St. Bartholomew's Hospital. 34 Upper Hamilton-terrace. N.W.

† Rutherford, William, M.D. F.R.S.E. Professor of Physiology in the Univ. of Edinburgh. The University; and 14 Douglas crescent, Edinburgh.


† Schäfer, Edward Albert, M.R.C.S. Jodrell Professor of Physiology, University College, London. Crowley Green, Rickmansworth.

† Schunck, Edward, F.C.S. Keral, Manchester.

R. * Schuster, Arthur, Ph.D. F.R.A.S. Professor of Physics in Owens College, Victoria University, Manchester. 4 Anson-road, Victoria-park, Manchester.


FELLOWS OF THE SOCIETY. (Nov. 30, 1885.)

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Selwyn, Alfred Richard Cecil, C.M.G. F.G.S. Late Director of the Geological Survey of Canada. Sussex-street, Ottawa, Canada.


† Sharp, William, M.D. F.G.S. Horton House, Rugby.


* Sherrington, Charles Scott, M.A. M.D. (Camb.) Professor of Physiology in University College, Liverpool. 16 Grove-road, Liverpool.


Simpson, Maxwell, B.A. M.B. M.D. & LL.D. (Hon. Dubl.) F.C.S. D.Sc. F.I.C. Hon. F.K.Q.C.P. (Dubl.) Late Professor of Chemistry in Queen's College, Cork. Late Fellow of the Royal University of Ireland. 9 Barton-street, West Kensington, W.


* Sollas, William Johnson, D.Sc. (Camb.) LL.D. (Dubl.) F.R.S.E. F.G.S. Professor of Geology in the University of Dublin. Lisnabín, Dartry-park-road, Rathgar, Dublin.

* Sprengel, Hermann Johann Philipp, Ph.D. (Heidelb.) F.C.S. Royal Prussian Professor (titular). Savile Club, 107 Piccadilly, W.

† Sprengel, Hermann Johann Philipp, Ph.D. (Heidelb.) F.C.S. Royal Prussian Professor (titular). Savile Club, 107 Piccadilly, W.

* Stirling, Edward Charles, C.M.G. M.A. M.D. (Camb.) F.R.C.S. C.M.Z.S. Senior Surgeon, Adelaide Hospital; Lecturer on Physiology in the University of Adelaide; Hon. Director of the South Australian Museum. The University, Adelaide, South Australia.
<table>
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<tr>
<th>Date of Election</th>
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<th>FELLOWS OF THE SOCIETY. (Nov. 30, 1895)</th>
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<tbody>
<tr>
<td>June 6, 1861.</td>
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<td>† Stoney, George Johnstone, M.A. D.Sc. Vice-President R.D.S. F.R.A.S. 8 Upper Horseley-rise. N.</td>
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<tr>
<td>June 1, 1854.</td>
<td>'72-'74</td>
<td>† Strauchey, Richard, Lieut.-General, R.E. C.S.I. LL.D. (Cantab.) V.P.R.G.S. F.G.S. F.L.S. Chairman Meteorological Council. 69 Lancaster-gate, Hyde-park. W.</td>
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<td>Date of Election</td>
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FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)

* Veley, Victor Herbert, M.A. F.C.S. University College; and 22, Norham-road, Oxford.
† Verdon, The Hon. Sir George Frederic, C.B. K.C.M.G. The Melbourne Club, Melbourne, Australia; and Athenæum Club, S.W.
Walker, James Thomas, General, C.B. R.E. LL.D. F.R.G.S. 13 Cromwell-road, South Kensington, S.W.
* Waller, Augustus Désiré, M.D. Lecturer on Physiology at St. Mary’s Hospital Medical School. 16 Grove End-road, N.W.
* Warington, Robert, M.A. (Oxon.) F.C.S. Sibthorpiian Professor of Rural Economy in the University of Oxford. High Bank, Harpenden, St. Albans.
* Warren, Sir Charles, Major-General, R.E. K.C.B. G.C.M.G. Government House, Chatham; and Athenæum Club, S.W.

Date of Election. | Served on Council.
---|---
June 7, 1877. | '90-'91
June 8, 1871. |
June 4, 1886. | '93-'94
June 7, 1894. |
June 7, 1883. |
June 2, 1870. |
June 4, 1885. | '90-'92
June 1, 1885. | '85-86 '90-'92
June 7, 1883. |
June 1, 1893. |
June 2, 1892. |
Nov. 22, 1860. |
June 9, 1887. |
June 7, 1888. | R.
June 4, 1886. |
June 12, 1881. |
June 2, 1881. |
FELLOWS OF THE SOCIETY. (Nov. 30, 1895.)

* Weldon, Walter Frank Raphael, M.A. Fellow of St. John's College, Jodrell Professor of Comparative Anatomy and Zoology at University College, London. 30a Wimpole-street. W.


Williams, C. Greville, F.C.S. F.I.C. Castlemaine, Oakhill-road, Putney. S.W.


† Wilson, George Fergusson, F.C.S. F.L.S. Heatherbank, Weybridge Heath, Surrey.


* Worthington, Arthur Mason, M.A. F.R.A.S. Headmaster and Professor of Physics, Royal Naval Engineering College, Devonport. 6 Osborne Villas, Debenport.

* Yeo, Gerald Francis, M.D. (Dublin) F.R.C.S. Emeritus Professor of Physiology in King's College, London. Bowden, Totnes, South Devon.

* Young, Sydney, D.Sc. (Lond.) F.C.S. F.I.C. Professor of Chemistry in University College, Bristol. 13 Aberdeen-road, White Ladies' road, Bristol.

† Younghusband, Charles Wright, Lieut.-General, C.B. Palace-court-mansions, Bayswater-road, W.; and Athenæum Club. S.W.
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FELLOWS DECEASED SINCE THE LAST ANNIVERSARY (Nov. 30, 1894).

On the Home List.

Aberdare, Henry Austin Bruce, Lord, G.C.B.
Babington, Charles Cardale, M.A.
Ball, Valentine, C.B.
Beetham, Albert William.
Bristowe, John Syer, M.D.
Buchanan, Sir George, M.D.
Carter, Henry John, Surgeon-Major.
Cayley, Arthur, D.C.L.
Cockle, Sir James, M.A.
Dobson, George Edward, M.A.

Hawkins, Bisset, M.D.
Hulke, John Whitaker, P.R.C.S.
Huxley, Right Hon. Thomas Henry, D.C.L.
Kirkman, Rev. Thomas Penyngton, M.A.
Rawlinson, Sir Henry Creswick, Bart., G.C.B.
Savory, Sir William Seovell, Bart.
Selborne, Roundell Palmer, Earl of.
Tomes, Sir John F.R.C.S.
Williamson, William Crawford, L.L.D

On the Foreign List.

Baillon, Henri Ernest.
Dana, James Dwight.
Lovén, Sven Ludwig.
Ludwig, Carl.

Neumann, Franz Ernst.
Pasteur, Louis.
Tchebitchef, Pafnutij.

Change of Name and Title.

Worms, Baron Henry de, to Lord Pirbright.

FELLOWS ELECTED SINCE THE LAST ANNIVERSARY.


## NAMES OF PERSONS TO WHOM THE MEDALS OF THE ROYAL SOCIETY HAVE BEEN AWARDED.

### Copley Medal

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COPLEY MEDAL—continued.

1840. Justus Liebig.
Jacques Charles François Sturm.
1841. George Simon Ohm.
1843. Jean Baptiste Dumas.
1844. Carlo Matteucci.
1845. Theodor Schwann.
1847. Sir John Frederick William Herschel.
1848. John Conch Adams.
1849. Sir Roderick Impey Murchison.
1850. Peter Andreas Hansen.
1851. Richard Owen.
1852. Baron Alexander von Humboldt.
1853. Heinrich Wilhelm Dove.
1854. Johannes Müller.
1858. Sir Charles Lyell.
1859. Robert Wilhelm Bunsen.
1860. Louis Agassiz.
1861. Thomas Graham.
1862. Rev. Adam Sedgwick.
1863. Charles Darwin.
1864. Michel Chasles.
1865. Julius Plücker.
1866. Karl Ernst von Baer.
1867. Sir Charles Lyell.
1869. Sir Charles Wheatstone.
1871. Robert Louis Pasteur.
1874. Robert Wilhelm Bunsen.
1875. Louis Pasteur.
1876. August Wilhelm Hofmann.
1877. Claude Bernard.
1879. Jean Baptiste Bonnionsault.
1880. James Joseph Sylvester.
1883. Sir William Thomson.
1884. Carl Ludwig.
1885. August Kekulé.
1886. Franz Ernst Neumann.
1887. Sir Joseph Dalton Hooker.
1888. Thomas Henry Huxley.
1889. Rev. George Salmon.
1890. Simon Newcomb.
1891. Stanislao Cannizzaro.
1892. Rudolf Virchow.
1893. Sir George Gabriel Stokes.
1894. Edward Frankland.
1895. Carl Weierstrass.

RUMFORD MEDAL.

1800. Benjamin Count Rumford.
1804. John Leslie.
1805. William Murdoch.
1810. Etienne Louis Malus.
1824. Augustin Jean Fresnel.
1826. John Frederic Daniell.
1828. Macedonio Melloni.
1840. Jean Baptiste Biot.
1842. Henry Fox Talbot.
1846. Michael Faraday.
1848. Henri Victor Regnault.
1850. François Jean Dominique Arago.
1852. George Gabriel Stokes.
1856. Louis Pasteur.
1890. James Clerk Maxwell.
1894. John Tyndall.
1898. Ralfour Stewart.
1870. Alfred Olivier Des Cloizeaux.
1874. Joseph Norman Lockyer.
1878. Alfred Cornu.
1880. William Huggins.
1884. Tobias Robertus Thalén.
1886. Samuel Pierpont Langley.
1888. Pietro Tacchini.
1890. Heinrich Hertz.
1892. Nils C. Dahlv.
ROYAL MEDAL.

1826. John Dalton.
   James Ivory.
1827. Sir Humphry Davy.
   Friedrich Georg Wilhelm Struve.
1828. Johann Friedrich Eucken.
   William Hyde Wollaston.
1829. Charles Bell.
   Eilhard Mitscherlich.
1830. David Brewster.
   Antoine Jerome Balard.
1831. Auguste Pyrame De Candolle.
   Sir John Frederick William Herschel.
   Charles Lyell.
1833. Michael Faraday.
   Sir William Rowan Hamilton.
1834. George Newport.
   Sir John F. W. Herschel.
1836. Thomas Graham.
   Henry Fox Talbot.
1837. James Ivory.
   Dr. Martin Barry.
1838. Sir John F. W. Herschel.
   Charles Wheatstone.
1839. Robert Kane.
   Eaton Hodgkinson.
1840. William Bowman.
   John Frederic Daniell.
   Charles Wheatstone.
1842. Thomas Andrews.
   George Boole.
1843. George Biddell Airy.
   Thomas Snow Bedd.
1844. Michael Faraday.
   Richard Owen.
1845. George Townes.
   William Robert Grove.
1846. Thomas Galloway.
   Charles James Hargreave.
1847. Colonel Edward Sabine.
   Gideon A. Mantell.
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   Thomas Henry Huxley.
1851. Charles Darwin.
   Angst Wilhelm Hofmann.
   Joseph Dalton Hooker.
1852. John Russell Hind.
   John Obadiah Westwood.
1853. Sir John Richardson.
   William Thomson.
1854. Edward Frankland.
   John Lindley.
1855. Albany Hancock.
   William Lassell.
1856. George Bentham.
   Arthur Cayley.
1857. William Fairbairn.
   Augustus Waller.
1858. William B. Carpenter.
   James Joseph Sylvester.
   Alexander William William.
   Sir William Logan.
   John Peter Gassiot.
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   Warren De La Rue.
   Archibald Smith.
1863. William Huggins.
   William Kitchen Parker.
1864. John Bennet Lawes and Joseph Henry Gilbert.
   Sir William Logan.
1865. Alfred Russel Wallace.
   Rev. George Salmon.
1866. Sir Thomas Maclear.
   Augustus Matthiessen.
1867. William Hallowes Miller.
   Thomas Davidson.
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   Henry John Carter.
1870. George James Allman.
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1871. Sir C. Wyville Thomson.
1872. Frederick Augustus Abel.
   Oswald Heer.
1873. Edward Horsley.
   Robert Archibald Horsley.
1874. Henry Clifton Sorby.
   William Crawford Williamson.
1875. William Crookes.
   Thomas Oldham.
1876. William Froude.
   Sir W. Wyville Thomson.
1877. Frederick Augustus Abel.
   Oswald Heer.
   Albert C. L. G. Günther.
1879. William Henry Ferkin.
   Andrew Crompton Ramsay.
   Andrew Noble.
1881. Francis Maitland Balfour.
   John Hewitt Jellett.
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   Lord Rayleigh.
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1884. George Howard Darwin.
   Daniel Oliver.
1885. David Edward Hughes.
   Edwin Ray Lankester.
1886. Francis Galton.
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   Harry Marshall Ward.
   Joseph John Thomson.
1895. James Alfred Ewing.
   John Murray.
DAVY MEDAL.

1877. Robert Wilhelm Bunsen.
       Gustav Robert Kirchhoff.
1878. Louis Paul Cailletet.
       Raoul Pictet.
1879. Paul Emile Lequeu de Boisbaudran.
1880. Charles Friedel.
1881. Adolf Baeyer.
1882. Dimitri Ivanovitch Mendeleeff.
       Lothar Meyer.
1883. Marcellin Berthelot.
       Julius Thomsen.

1885. Jean Servais Stas.
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1888. William Crookes.
1889. William Henry Perkin.
1890. Emil Fischer.
1891. Victor Meyer.
1892. Francois Marie Raoult.
1893. J. H. van't Hoff.
       J. A. Le Bel.
1894. Per Theodor Cleve.
1895. William Ramsay.

DARWIN MEDAL.

1890. Alfred Russel Wallace.
1892. Sir Joseph Dalton Hooker.
1894. Thomas Henry Huxley.
ADVERTISEMENT.

The Committee appointed by the Royal Society to direct the publication of the Philosophical Transactions take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former Transactions, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the Transactions had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind: the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future Transactions; which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body,
upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report, and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.
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" " B " " " " Series B, and Proceedings.

" " AB " " Proceedings only.

Series A and B, and Proceedings.

America (Central).

Mexico.
p. Sociedad Cientifica "Antonio Alzate."

America (North), (See United States and Canada.)

America (South).

Buenos Ayres.
AB. Museo Nacional.

Caracas.
b. University Library.

Cordova.
AB. Academia Nacional de Ciencias.

Demerara.

La Plata.
b. Museo de La Plata.

Rio de Janeiro.
p. Observatorio.

Australia.

Adelaide.
p. Royal Society of South Australia.

Brisbane.

Melbourne.
p. Observatory.
AB. University Library.

Sydney.
p. Linnean Society of New South Wales.
AB. Royal Society of New South Wales.
AB. University Library.

Austria.

Agram.

MDCCXCIV.—A.

Austria (continued).

Brünn.
AB. Naturforschender Verein.

Gratz.
AB. Naturwissenschaftlicher Verein für Steiermark.

Innsbruck.
AB. Das Ferdinandeum.

Prague.
AB. Königliche Böhmische Gesellschaft der Wissenschaften.

Trieste.
b. Museo di Storia Naturale.
p. Società Adriatica di Scienze Naturali.

Vienna.
p. Anthropologische Gesellschaft.
AB. Kaiserliche Akademie der Wissenschaften.
AB. K.K. Geologische Reichsanstalt.
b K.K. Naturhistorisches Hof-Museum.
p. Oesterreichische Gesellschaft für Meteorologie.
A. Von Kuffner’sche Sternwarte.

Belgium.

Brussels.
b. Académie Royale de Médecine.
AB. Académie Royale des Sciences.
b. Musée Royal d'Histoire Naturelle de Belgique.
p. Observatoire Royal.
p. Société Belge de Géologie, de Paléontologie, et d'Hydrologie.
p. Société Malacologique de Belgique.

Ghent.
AB. University.
Belgium (continued).

Cooper’s Hill.
  AB. Royal Indian Engineering College.

Dudley.

Essex.
  p. Essex Field Club.

Falmouth.
  p. Royal Cornwall Polytechnic Society.

Greenwich.
  a. Royal Observatory.
  b. Royal Gardens.

Leeds.
  p. Philosophical Society.
  AB. Yorkshire College.

Liverpool.
  AB. Admiralty.
  AB. British Museum (Nat. Hist.).
  AB. Chemical Society.
  a. City and Guilds of London Institute.
  p. “Electrician,” Editor of the.
  b. Entomological Society.
  AB. Geological Society.
  AB. Geological Survey of Great Britain.
  AB. Guildhall Library.
  a. Institution of Civil Engineers.
  p. Institution of Electrical Engineers.
  a. Institution of Mechanical Engineers.
  a. Institution of Naval Architects.
  AB. King’s College.
  a. Linnean Society.
  AB. London Institution.
  p. Meteorological Office.
  p. Odontological Society.
  p. Physical Society.
  p. Quekett Microscopical Club.
  b. Royal College of Physicians.
  b. Royal College of Surgeons.

Canada.

Hamilton.

Montreal.
  AB. McGill University.
  p. Natural History Society.

Ottawa.
  AB. Geological Survey of Canada.
  AB. Royal Society of Canada.

Toronto.
  p. Canadian Institute.
  AB. University.

Cape of Good Hope.

  a. Observatory.
  AB. South African Library.

Ceylon.

  Colombo.
  b. Museum.

China.

  Shanghai.

Denmark.

  Copenhagen.
  AB. Kongelige Danske Videnskabernes Selskab.

Egypt.

  Alexandria.
  AB. Bibliothèque Municipale.

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Aberystwith.
  AB. University College.

Bangor.
  AB. University College of North Wales.

Birmingham.
  AB. Free Central Library.
  AB. Mason College.
  p. Philosophical Society.

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  p. Public Library.

Bristol.
  AB. University College.

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  AB. Philosophical Society.
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London (continued).
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  p. Royal Horticultural Society.
  p. Royal Institute of British Architects.
  ab. Royal Institution of Great Britain.
  b. Royal Medical and Chirurgical Society.
  p. Royal Meteorological Society.
  p. Royal Microscopical Society.
  ab. Royal United Service Institution.
  ab. Society of Arts.
  p. Society of Biblical Archaeology.
  p. Standard Weights and Measures Department.
  ab. The Queen's Library.
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  ab. University College.
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  ab. Free Library.
  ab. Literary and Philosophical Society.
  ab. Owens College.
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  p. Royal Victoria Hospital.
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  ab. Free Library.
  p. Society of Chemical Industry (Newcastle Section).
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  p. Norfolk and Norwich Literary Institution.
Nottingham.
  ab. Free Public Library.
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  ab. Radcliffe Library.
   a. Radcliffe Observatory.
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   p. Plymouth Institution.
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  p. The College.
Swansea.
  ab. Royal Institution.
Woolwich.
  ab. Royal Artillery Library.
Finland.
Helsingfors.
  p. Societas pro Fauna et Flora Fennica.
  ab. Societe des Sciences.
France.
Bordeaux.
  p. Faculté des Sciences.
  p. Société de Médecine et de Chirurgie.
 Cherbourg.
Dijon.
Lille.
  p. Faculté des Sciences.
Lyons.
  ab. Académie des Sciences, Belles-Lettres et Arts.
  ab. Université.
Marseille.
  p. Faculté des Sciences.
Montpellier.
  ab. Académie des Sciences et Lettres.
   b. Faculté de Médecine.
Nantes.
Paris.
  ab. Académie des Sciences de l'Institut.
   p. Commission des Annales des Ponts et Chaussées.
  p. Conservatoire des Arts et Métiers.
  ab. Dépôt de la Marine.
   ab. École des Mines.
   ab. École Normale Supérieure.
   ab. École Polytechnique.
   ab. Faculté des Sciences de la Sorbonne.
   ab. Jardin des Plantes.
   p. L'Électricien.
France (continued).

Paris (continued).

a. L’Observatoire.
ab. Société de Biologie.
ab. Société de Géographie.
p. Société de Physique.
b. Société Entomologique.
ab. Société Géologique.

Toulouse.
ab. Académie des Sciences.
a. Faculté des Sciences.

Germany.

Berlin.
a. Deutsche Chemische Gesellschaft.
a. Die Sternwarte.
ab. Königliche Preussische Akademie der Wissenschaften.
a. Physikalische Gesellschaft.

Bonn.
ab. Universität.

Bremen.

Breslau.
p. Schlesische Gesellschaft für Vaterländische Kultur.

Brunswick.

Karlsruhe. See Karlsruhe.

Charlottenburg.
a. Physikalisch-Technische Reichsanstalt.

Danzig.
ab. Naturforschende Gesellschaft.

Dresden.
p. Verein für Erdkunde.

Emden.

Erlangen.
ab. Physikalisch-Medicinische Societät.

Frankfurt-am-Main.
ab. Senckenbergische Naturforschende Gesellschaft.

Frankfurt-am-Oder.

Freiburg-im-Breisgau.
ab. Universität.

Giessen.
ab. Grossherzogliche Universität.

Germany (continued).

Görlitz.

Göttingen.
ab. Königliche Gesellschaft der Wissenschaften.

Halle.
ab. Kaiserliche Leopoldino - Carolinische Deutsche Akademie der Naturforscher.

Hamburg.
ab. Naturwissenschaftlicher Verein.

Heidelberg.
ab. Universität.

Jena.
ab. Medicinisch-Naturwissenschaftliche Gesellschaft.

Kiel.
a. Sternwarte.
ab. Universität.

Königsberg.
ab. Königliche Physikalisch - Ökonomische Gesellschaft.

Leipsic.
a. Astronomische Gesellschaft.
ab. Königliche Sächsische Gesellschaft der Wissenschaften.

Magdeburg.

Marburg.
ab. Universität.

Munich.
ab. Königliche Bayerische Akademie der Wissenschaften.

Münster.
ab. Königliche Theologische und Philosophische Akademie.

Potsdam.
a. Astrophysikalisches Observatorium.

Rostock.
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Strasburg.
ab. Universität.

Tübingen.
ab. Universität.
Germany (continued).

Würzburg.
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Greece.

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A. National Observatory.

Holland. (See Netherlands.)

Hungary.

Buda-pest.
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Hermannstadt.
p. Siebenbürgischer Verein für die Naturwissenschaften.

Klausenburg.
AB. Az Erdélyi Muzeum. Das Siebenbürgische Museum.

Schemnitz.

India.

Bombay.
AB. Elphinstone College.
p. Royal Asiatic Society (Bombay Branch).

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AB. Asiatic Society of Bengal.
AB. Geological Museum.
p. Great Trigonometrical Survey of India.
AB. Indian Museum.
p. The Meteorological Reporter to the Government of India.

Madras.
b. Central Museum.
a. Observatory.

Roorkee.
p. Roorkee College.

Ireland.

Armagh.
a. Observatory.

Belfast.
AB. Queen's College.

Cork.
p. Philosophical Society.
AB. Queen's College.

Dublin.
a. Observatory.
AB. National Library of Ireland.
b. Royal College of Surgeons in Ireland.
AB. Royal Dublin Society.
AB. Royal Irish Academy.

Galway.
AB. Queen's College.

Italy.

Acireale.

Bologna.
AB. Accademia delle Scienze dell' Istituto.

Catania.
AB. Accademia Gioenia di Scienze Naturali.

Florence.
AB. Museo Botanico.
p. Reale Istituto di Studi Superiori.

Genoa.
p. Società Ligustica di Scienze Naturali e Geografiche.

Milan.
AB. Società Italiana di Scienze Naturali.

Modena.
p. Le Stazioni Sperimentali Agrarie Italiane.

Naples.
p. Società di Naturalisti.
AB. Società Reale, Accademia delle Scienze.
E. Stazione Zoologica (Dr. Dohrn).

Padua.

Palermo.
A. Circolo Matematico.
AB. Consiglio di Perfezionamento (Società di Scienze Naturali ed Economiche).
A. Reale Osservatorio.

Pisa.
p. Società Toscani di Scienze Naturali.

Rome.
a. Reale Ufficio Centrale di Meteorologia e di Geodinamica, Collegio Romano.
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p. R. Comitato Geologico d' Italia.
a. Specola Vaticana.
AB. Società Italiana delle Scienze.

Siena.

Turin.
AB. Reale Accademia delle Scienze.

Venice.
p. Ateneo Veneto.
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<thead>
<tr>
<th>Country</th>
<th>City</th>
<th>Institution</th>
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<td>Japan</td>
<td>Tokio</td>
<td>Imperial University</td>
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|                | Madrid.  
|                | P. Comisión del Mapa Geológico de España.                                     |
|                | AB. Real Academia de Ciencias.                                                |
| Sweden         | Gotenburg.  
|                | AB. Kongl. Vetenskaps och Vitterhets Samhäll.                                 |
|                | Lund.  
|                | AB. Universitets.                                                            |
|                | Stockholm.  
|                | A. Acta Mathematica.                                                         |
|                | AB. Kongliga Svenska Vetenskaps-Akademien.                                   |
|                | AB. Sveriges Geologiska Undersökning.                                        |
|                | Upsala.  
|                | AB. Universitet.                                                             |
| Switzerland    | Basel.  
|                | P. Naturforschende Gesellschaft.                                              |
|                | Bern.  
|                | AB. Allg. Schweizerische Gesellschaft.                                       |
|                | P. Naturforschende Gesellschaft.                                              |
|                | Geneva.  
|                | AB. Société de Physique et d'Histoire Naturelle.                            |
|                | AB. Institut National Genevois.                                               |
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|                | P. Société Vandoise des Sciences Naturelles.                                 |
|                | Neuchâtel.  
|                | P. Société des Sciences Naturelles.                                           |
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|                | P. Naturforschende Gesellschaft.                                              |
|                | P. Sternwarte.                                                                |
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|                | P. Royal Society of Tasmania.                                                 |
| United States  | Albany.  
|                | AB. New York State Library.                                                   |
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|                | AB. Naval Academy.                                                           |
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|                | P. Texas Academy of Sciences.                                                 |
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|                | Berkeley.  
|                | P. University of California.                                                  |

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|                | Chapel Hill (N.C.).                                                          |
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|                | P. Journal of Comparative Neurology.                                           |
|                | Davenport (Iowa).                                                            |
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|                | P. Physical Review (Cornell University).                                      |
|                | Madison.  
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|                | Mount Hamilton (California).                                                  |
|                | A. Lick Observatory.                                                         |
|                | New Haven (Conn.).                                                           |
|                | AB. American Journal of Science.                                              |
|                | AB. Connecticut Academy of Arts and Sciences.                                 |
|                | New York.  
|                | P. American Geographical Society.                                             |
|                | P. American Museum of Natural History.                                       |
|                | P. New York Academy of Sciences.                                              |
|                | P. New York Medical Journal.                                                   |
|                | P. School of Mines, Columbia College.                                         |
|                | Philadelphia.                                                                |
|                | AB. Academy of Natural Sciences.                                              |
|                | AB. American Philosophical Society.                                           |
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|                | P. Academy of Science.                                                        |
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|                | AB. Essex Institute.                                                          |
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  A. Patent Office.
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  E. United States Geological Survey.

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By C. V. Boys, A.R.S.M., F.R.S., Assistant Professor of Physics, Royal College of Science, South Kensington.

Received May 31,—Read June 7,—Revised October 18, 1894.

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PART I.

Preliminary.

In a paper on the Cavendish experiment, published in the 'Proc. Roy Soc.' vol. 46, p. 253, I showed how the famous experiment of Cavendish* could be transformed in several particulars, so that greatly increased delicacy and accuracy would be obtainable.

The experiment is so well known that there is no occasion to describe the apparatus which Cavendish employed, or the subsequent work of Reich,† Baily,‡ or Cornu and Baille.§ It is sufficient to state that, owing to the extremely small value of the Newtonian constant of gravitation, all these experimenters made use of balls as large as they conveniently could, so as to increase the force of attraction as much as possible, and of a lever as long as they could, so as to increase the effect of the force in producing torsion. However, Cornu realized that if he could keep the period the same by the use of a sufficiently fine torsion wire, and reduce the dimensions of the whole apparatus, the angle of deflection would not be reduced but would remain the same. Cornu also introduced refinements which have made the behaviour of his apparatus far more consistent than that of any which had preceded it.

Soon after I had made and found the value of quartz fibres for producing a very small and constant torsion, I thought that it might be possible to apply them to the Cavendish apparatus with advantage, which opinion I found was also held by Professor Tyndall. Before employing them for this purpose I examined the theory of the apparatus with a view to using them in the most suitable manner.

The sensibility of this kind of apparatus is, if the period is maintained always the same, independent of its linear dimensions; for in two similar instruments, in which all the dimensions of one are \( n \) times the corresponding dimensions of the other, the moments of inertia of the beams and their appendages are as \( n^5 : 1 \); and, therefore, if the period is to be unchanged, the torsional couples must be as \( n^5 : 1 \) also. The attracting masses, both fixed and movable, are as \( n^5 : 1 \), and their distances apart as \( n : 1 \); therefore, the attractions are as \( n^5/n^2 \), or as \( n^3 : 1 \), and these, acting on arms \( n \) times as long in one as in the other, produce moments as \( n^5 : 1 \); that is, in the same proportion as the torsional rigidities, and so the angles of deflection are the same in the two cases.

If, however, the length of the beam only is changed, and the attracting masses are moved until they are opposite to and a fixed distance from the ends of the beam, then the moments of inertia will be altered in the ratio \( n^2 : 1 \), while the corresponding moments will only change in the ratio \( n : 1 \), and thus there is an advantage in reducing the length of the beam until one of two things happens, either it is difficult to find a sufficiently fine torsion thread that will safely carry the beam and produce the required period—and this, no doubt, has prevented the use of a beam less than that

* 'Phil. Trans.' 1798, p. 469.
† 'Comptes Rendus,' 1837, p. 697.
‡ 'Phil. Mag.,' vol. 21, 1842, p. 111.
half a metre in length—or else, when the length becomes nearly equal to the diameter of the attracting balls, they then act with such an increasing effect on the suspended balls at the other end of the beam, that the balance of effect begins to fall short of that which would be due to the reduced dimensions if the opposite ball did not interfere.

I showed, in the paper already referred to, that when the attracting balls have been brought as near to the equatorial plane, or plane perpendicular to the length of the beam, as they are to the plane of the beam, so that the line joining them makes an angle of 45° with the beam, that is that the azimuth is 45°, the ultimate sensibility is still further increased by shortening the beam to half the length that would bring the ends opposite the attracting balls. After that the sensibility very slowly begins to fall.

Since, with such small apparatus as the quartz fibre seemed to make practicable, it is easy to provide attracting masses which are very large in proportion to the length of the beam, while with the usual long beam relatively small masses must be made use of, it is clear that much greater deflections can be produced with small than with large apparatus. For instance, to obtain the same effect in the same time in an instrument with a 6-foot beam that I was able to realize in my preliminary apparatus, in which the beam was $\frac{3}{4}$ inch in length, as seen from above, with attracting balls 2 inches in diameter, it would be necessary to provide and deal with a pair of balls each 25 feet in diameter, and weighing 730 tons, instead of about 1 2 lb. apiece. There is the further advantage in small apparatus that if, for any reason, the greatest possible effect is desired, attracting balls of gold would not be entirely unattainable.

The use of attracting balls which are themselves very large compared with the beam length makes it convenient to hang the beam in a cylindrical tube, instead of in the long box almost universally employed hitherto. Several advantages follow from this. In the first place, if the beam is hung centrally, neither the gravitational attraction of the tube nor any minute difference of potential between the tube and the beam and its accessories, produce any effect. In the second place, the attracting balls may be carried round outside the tube through a complete circle, and yet be placed but little further from the attracted balls than would be necessary if no intervening tube existed. For this purpose they are conveniently supported by a common metallic structure, symmetrical in form, about the axis of the tube, and able to rotate about this axis also. If, following the usual arrangement, all four balls are on one level, there are obviously two planes, one containing and one normal to the beam, in which the centres of the attracting balls may be placed so as to produce no deflection. At some intermediate position the deflection will be a maximum. The use of this position has the obvious advantage that, besides the fact that this gives the greatest effect, the accuracy with which the angle of azimuth is measured is of little consequence, the geometrical measurements of real importance being the distance between the centres of the large balls, the corresponding distance between the centres of the small balls, and the angle of deflection. This is all the more important since it would be extremely difficult to make a really accurate determination of the azimuth,
whereas the other three quantities can be measured, as will appear later, with the highest degree of precision.

It will be evident that, as the size of the attracting balls is increased with the object of increasing the deflection, their action on the opposite suspended balls increases in a very high ratio, so that very soon a practical limit is reached, beyond which any increase of size produces an insignificant effect. For instance, if the distance between the centres of the attracting balls is five times the length of the beam, and they are set at the angle (58° 20') at which their action is a maximum, the counteracting couple due to the far ball is $\frac{1}{3}$ of that due to the near one, so that the resultant couple is only $\frac{3}{4}$ of that which would be produced if the attraction on the remote end of the beam could be annulled. This, in effect, I practically accomplished by arranging the two sides of the apparatus at very different levels. In this way, if only the exact position of the balls can be determined, or rather their co-ordinates can be ascertained with degrees of accuracy in proportion to their importance, then the arrangement is eminently suitable for the purpose of finding the gravitation constant.

The preliminary apparatus that I made on this principle in 1889 worked so well, even under the unfavourable conditions met with at South Kensington, that I felt satisfied that an instrument built on the same lines, but in which the necessary geometrical measurements could be made, would enable me to make a more accurate measure of the Newtonian constant than had been considered possible hitherto. I even felt satisfied that it could be determined with an accuracy of 1 in 10,000; and this extreme degree of precision I now feel certain may be attained by a skilled experimentalist, if the very small modifications suggested by my recent work, which are described at the end of this paper, are adopted, and if, above all, the experimentalist, whoever he may be, has time and place at his command, and is not driven by necessity to steal as much time for observation from his holidays and nights as his physical strength will allow.

In the design of any apparatus, it is necessary to have some definite idea as to the degree of accuracy which is to be aimed at, so that trouble may not be taken in attaining an absurd degree of precision in one part, while some other part is glaringly in defect. The aim which I made, and which my preliminary experiments showed to be reasonable, was one of 1 in 10,000 in the result; for this purpose the large masses would have to be determined

\[
\text{to } 1 \text{ in } 10,000; \\
times \text{, } 1 \text{, } 20,000; \\
some \text{ lengths } \times \text{, } 1 \text{, } 20,000 \text{ about}; \\
other \times \text{, } 1 \text{, } 10,000; \\
an \text{ angle } \times \text{, } 1 \text{, } 10,000.
\]

I gathered from conversation with some physicists of note, whose judgment and experience I fully appreciated, that there was some doubt whether I was doing right in persisting in making small apparatus where absolute determinations were the object, for though I had clearly enough shown that so far as sensibility and constancy
of deflection and period were concerned an advantage could so be obtained, it did not at all follow that I should be able to determine the geometry of small apparatus with sufficient accuracy. Of course, as the apparatus is made smaller, this difficulty necessarily increases.

If in the apparatus upon which I have finally decided the angular deflections and squares of the periods can be determined with greater proportionate accuracy than the masses or lengths, or lengths squared, as the case may be, then I have gone too far, and the apparatus is too small, but if, as I expect to satisfactorily prove in this paper, my geometry and weighings (of course, the latter) are well in excess of the deflections and squares of the periods in point of accuracy, then I maintain that I am justified in having acted up to my principles, even though I did so in opposition to the views which I heard expressed.

There is one point referred to (p. 258), but not sufficiently in detail, in my paper already quoted which I should like to develop, more especially as Professor Poynting* has noticed it, and has, I think, agreed with my conclusion. At the same time I owe to him the discovery of a mistake which I made which led me to attribute too high an importance to the advantage of smallness from this point of view. What follows is the result of a discussion, which I took the opportunity of entering upon while travelling recently with Professor Poynting. The point is, that the disturbances due to convection are likely to be relatively of less importance in small than in large apparatus, even though the period is maintained the same. As convection disturbances are those which are the last and the most difficult to avoid, and as I feel sure that they set the limit to the accuracy that is obtainable in this experiment, and that discrepancies attributed to silk, or even to quartz fibres, and to other causes, are in many physical investigations simply due to convection, I think that too much attention cannot be given to this part of the subject.

Let there be two pieces of apparatus, precisely similar in all respects, but with the linear dimensions in one 2\(n\) times those in the other, then when the pieces of apparatus are set up, they are subject under the best conditions to infinitesimal variations of temperature from the outside of two kinds; in the first, the surrounding space may not be uniform in temperature, it may be hotter on one side than on the other; in the other, the temperature, whether uniform or not, may slowly change from day to day.

In the first case the instruments may be considered as being placed in a region which would, but for their existence, possess a constant but very small temperature gradient. If an instrument be placed in such a region, the temperature gradient in the instrument will be also constant in certain cases, and will depend simply on the conductivity for heat of the material of which it is made and of the medium in which it is placed, but it will be independent of the linear dimensions. Further, whatever form a pair of similar instruments may have, the gradients at corresponding points in

each will be independent of the linear dimensions, and so the temperature differences of corresponding pairs of points or of the two sides will be proportional to \( n \). In consequence of this difference of temperature the included air will be warmer on one side than on the other and will circulate. The linear velocity of circulation will depend upon the difference of pressure between the ends of the upcast and downcast sides divided by the resistance due to viscosity, \( i.e., \) in such cases as we are concerned with, where the pressures and velocities are infinitesimal, and practically all the energy is expended in overcoming viscosity and none in imparting energy of motion to the gas.

The difference of pressure varies as the height multiplied by the difference of temperature, or as \( n^2 : 1 \). The effect of viscosity is proportional to the length of the channel, and inversely as its area; it varies, therefore, as \( n^{-1} : 1 \). The velocity of circulation will vary as \( n^2/n^{-1} \), or as \( n^3 : 1 \). In order to ascertain what disturbing effect this movement may have upon the suspended part of the apparatus, we may either consider that the force depends upon the product of the area into the velocity gradient or rate of shear of the surrounding air, \( i.e., \) that it is proportional to \( n^3 \times n^3 \), or \( n^4 \), in which case, since the force is to be multiplied by an arm also \( n \) times as long in order to obtain the couple, this becomes \( n^5 \); or without considering the velocity at all we may consider the suspension as part of the boundary of the gas receiving its share of the drag which is felt by the surrounding tube. The proportion must be the same in the two cases. The force causing the drag is proportional to the difference in temperature of the air columns multiplied by their area, or to \( n^4 \), and, therefore, the drag on the suspension varies as \( n^2 \) and the couple produced as \( n^5 \), as before. From this it would appear that no gain or loss results from a diminution of size. It must, however, be remembered, that, as apparatus is made larger, the three-fold increase in velocity in the air-current may well bring it up to such a value that its square can no longer be considered inappreciable. When the velocity is sufficient for the effect of impact to be felt, then the couple will follow a law depending upon a higher power of \( n \) than the fifth which, with increase of velocity, will approach the eighth power of the linear dimensions.

I do not anticipate with my design, which with its double tube and protecting screens is eminently favourable for the attainment of a uniform temperature in the inside, that the air velocity will ever approach that in which the square becomes appreciable, so that in a suitable underground observing room I should not expect any loss of definiteness to follow a moderate increase of size; nevertheless, I should feel doubtful as to the result if the dimensions were increased inordinately. Practically, however, smallness has a very great advantage, owing to the length of time which must elapse between the carrying out of any operation in which the apparatus is handled or otherwise warmed by manipulation, and its acquiring such a steady state again as to be fit for the observer to make the delicate observations of the movements of the suspended system. I have even considered three days to be necessary for my small apparatus to be ready for observation of deflection and period after making the
NEWTONIAN CONSTANT OF GRAVITATION.

micrometric observation. This, in fact, corresponds, but not exactly, with the second case mentioned above, where a gradual change of temperature is going on in the surrounding space; those parts of the apparatus that are massive will lag behind in temperature more than the lighter and thinner parts, and, as was pointed out by Cavendish, this is especially the case in apparatus for measuring the Newtonian constant of gravitation. The large lead balls are sure to be hotter or cooler than the light rectangular box, and, when hotter, by warming the side of the box near to them they set up a circulation, which, in the apparatus of Cavendish, produced an appearance of attraction.

If it is supposed that after all has acquired a uniform temperature a slight change occurs in the surrounding space, then the asymmetrical store of heat will, in the case of a large apparatus, be \( n^8 \) times as great as in the other. As before, the conductivity will be \( n \) times as great, so that an asymmetrical distribution of temperature will be \( n \) times as great, and will last \( n \) times as long in the large as in the small apparatus.

Before I come to describe the apparatus which forms the subject of the present paper, I wish to explain why I have employed what may appear objectionable, viz., mixed units. I applied to Mr. Chaney, at the Standards Office, for his opinion, as to the limit of accuracy with which he could verify certain lengths and masses. The lengths upon which the accuracy of the whole research would depend were to be of the order of 1 inch and 6 inches. If I could, as he considered certain, have them determined more accurately in relation to the standard 1-inch than I could in relation to the centimetre, it would be preferable to have the main dimensions of the apparatus set out in terms of the inch, and for construction in England there were practical advantages in adopting the inch system. On the other hand, the cathetometer that I used (Cambridge Scientific Instrument Co.'s), and the screw micrometer (Elliot), both of which were required to make measures of only secondary importance, were divided in centimetres. I have therefore had to make use of both kinds of measures, but have retained the inch as my standard. With respect to the masses, no difficulty could arise in obtaining the necessary accuracy, whether pounds or grammes were used. Having gramme weights I was led to make all the weighings in grammes, except where, owing to an insufficiency, I had to make up with a standard 7 lb. and 4 lb. weight belonging to the South Kensington Museum. These were determined in grammes, and expressed as such. Circumstances have therefore compelled me to carry out my experiments on the inch gramme second system, and this I have done, finally converting the values for \( G \) so found into the C.G.S. system, by multiplying by the number of cubic centimetres in a cubic inch. \((2.53995)^2 = 16.3861\).

As the suspended masses take up slightly different positions according as they are attracted by the large balls in one or the other direction, I was most careful in the design to arrange that the apparatus, with the exception of these balls, should be one
figure of revolution about the suspending fibre as an axis. With the hope of obtaining very perfectly conducting and uniform cylinders, both for the outer case and for the central tube, I ascertained what sizes of Elmore tube would be obtainable, and thus determined the actual and final dimensions of the apparatus. When this was too far advanced for change to be possible, the Elmore Company informed me that they could not supply the sizes previously settled, and so I had to be content with a piece of thick triblet-drawn brazed copper tube for the centre, and a thick brass casting for the surrounding case. The experiments show that no appreciable disturbance has arisen owing to any want of perfection in the tube. The casting was turned inside and out without being moved from the face plate, and, except in conductivity, is as perfect as pure copper. In order to keep the gravitational symmetry round the axis as perfect as possible, I had holes drilled in the massive base round the levelling screws, so as to remove as much metal as they added. The important dimensions on which I finally decided were:—

Distance from centre to centre of large balls in plan, 6 inches or 4 inches.
Distance from centre to centre of small balls in plan, 1 inch, about.
Diameter of large balls, 4\(\frac{1}{2}\) inches or 2\(\frac{1}{2}\) inches.
Diameter of small balls, 2 inch and 2\(\frac{1}{2}\) inch.
Difference of level between upper and lower pairs, 6 inches.

With these settled the rest of the design of the apparatus shown in figs. 1–15 followed naturally enough. I think it most convenient first to describe the apparatus in moderate detail, without going into the reasons why I decided upon each particular, and afterwards to show how the design accomplishes all that is needed for an accurate determination of G, the Newtonian constant of gravitation.

*The Apparatus* (Plate 1).

Fig. 1 is a vertical section through the centre of the apparatus, the window alone being in elevation; fig. 2 is a sectional plan through *aa*. Taking the structure first, B is a massive brass base, turned on both sides, carried by three levelling screws with lock nuts. C is the outer brass cylindrical casing screwed to the base B and accurately turned as already mentioned. L is a turned brass lid mechanically fitting C, on which it can be made to turn by the action of the train of wheels *WWW*. The edge of the flange is divided in degrees, and can be read to \(\frac{1}{10}^\circ\) upon the vernier *V*, fig. 3. Two tubular pillars PP are fitted into holes diametrically opposite to one another and 6 inches or 4 inches apart, according to the size of ball that is to be used. The heads of these pillars are shown half size in figs. 4, 5, 6, where it will be seen that at angles of 120\(\circ\) there are three radial *V*'s forming a geometrical clamp with either ball support. Also that on just raising the latter and giving it a rotation of 60\(\circ\) it can be let down through the tubular pillar. As seen, the large balls hang from these geometrical clamps by wires, but into these particulars and into the details
connected with the construction of the balls I shall enter later. The central tube T
is held accurately in its place by a cylindrical fitting and the hollow screw S. This
tube, up to the window just above the lid, is made of thick copper; at the window
level it is united by the window casting to the upper tube of the same size, which is
made of brass, and this carries at its upper end the torsion head surmounted by the
bell jar J with a central stop-cock. The torsion head admits of a variation of level
of about 2 inches and of horizontal adjustment by means of three screws. The
window casting forming the centre of the tube does not touch the lid, there being a
space of about \( \frac{1}{16} \) of an inch between them. The equality of this all round is
an excellent test of the accuracy of this part of the construction. The window is
shown half size in figs. 8, 9, and 10. Fig. 8 is a front view, the upper part being in
section, fig. 9 is a side view, and fig. 10 a section through \( aa \). The thick cylindrical
casting is cut through front and back so as to form two flat square faces FF 2 inches
in the side each, and over these 2 inches the casting is cut right through, forming
a square chamber in which the beam mirror hangs, and certain operations can be
carried on. Four milled heads \( h_1, h_2 \) are employed in making the transfer of the
smaller balls to and from the beam mirror, of which an enlarged view is shown in
fig. 7. This operation is performed as follows: the two heads \( h_1 \) are fixed to the
same cross axle, and when turned through a right angle cause two arms
with \( V \) notches at their ends to pick up the beam (fig. 7) by its upper cross
arms. In this way the beam can be raised or lowered a little or let down so
as to hang from its torsion fibre. The small balls hang by quartz fibres from the
hooks and eyes seen in fig. 7. When not on the beam these hang by their eyes from
the points projecting from the cranked ends of the pins operated by the heads \( h_1, h_2 \),
which can be turned or pushed in or drawn out. By combining the movement of
the heads \( h_1 \) and \( h_2 \) one of the hooks and eyes can be transferred to the \( V \) at the end
of the upper arm of the beam mirror resting there by its hook. In the same way
the other one is transferred. To prevent risk of the tipping of the beam and
fracture of the torsion fibre during this operation, a weight is first hung on to the
lower central hook of the beam and removed when the double operation is complete.
The ends of the mirror have very fine \( V \) grooves ground in them, so that the quartz
fibres hanging from the hooks may lie in these grooves and so be held definitely in
position, both with respect to their distance apart and circumferentially with
respect to the mirror. A cylindrical counter-weight K, fig. 7, of known very small
moment of inertia, but of exactly the same weight as the small balls with their hooks
and fibres, can be hung upon the central hook of the beam, when the balls are
removed to the side hooks, so that the fibre may be stretched to the same extent
and therefore have the same torsional rigidity when the periods are being taken with
or without the small pair of balls.
A series of windows are provided to fit upon and make an air-tight joint with the
plane-faces FF. Two are mere squares of plate-glass of the exact size needed. These
MDCCCXCV.
are used to protect the freely hanging mirror from draughts when observations are made upon it with the cathetometer. The window, fig. 11, is made of brass, electro-gilt, with a small aperture just large enough to allow the telescope T, figs. 18, 19, and all parts of the scale S, figs. 18, 21, to be seen from all parts of the mirror. The outer face of this window is covered with a plate of glass optically worked by Hilger, held in place by soft wax. The top and bottom sectors and the faces F F are smeared with vaseline to make an air-tight joint when the window is in position. The window, fig. 12, is made of brass, electro-gilt; it is similarly fixed in position behind the mirror. A brass tube, lightly filled with cotton-wool, screws into this window on one side. The window shown in vertical section, fig. 13 and in plan, fig. 14, is made of brass with a flat tubular opening with rounded ends. This enters the rectangular chamber and rests against the faces F F, which have been cut away at their lower part sufficiently for this purpose. The inner end of this tube is covered with a naturally cleaved thin film of mica, which enables the two quartz fibres hanging from the freely suspended mirror to be seen by two high-power microscopes whose noses penetrate into the flat tube without allowing them to be blown about by draughts. The use of mica for this purpose is essential. Mr. Cunynghame had previously shown me that the definition of a good telescope, which is absolutely destroyed by window glass held in front of it and impaired by any but perfect optically worked glass, is not affected by a leaf of mica, even though it may be bent or be apparently irregular. In the same way, the apparent position of anything seen by a microscope is altered if a piece of ordinary cover glass is placed between the two at some distance from the object, besides which the definition suffers. A thin leaf of mica in no way affects the definition or the apparent position, and so the distance apart of the fibres measured by the microscopes, as will be described later, is the true distance, which it never would be if cover glass were employed. This distance must be measured with the mirror freely hanging so that it may be the same as it is when the deflections, etc., are being observed.

Resting on the base B, fig. 1, are four india-rubber discs I R, with large central holes, their object being to form a soft cushion for the lead balls M M to rest upon when not suspended or to fall upon in case of accident.

In the same way I have provided a safety catch and recovering device in case the small balls should fall down the central tube. When the mirror is suspended and has been adjusted with its torsion fibre axial, the loss of time that would ensue if the little balls could only be recovered by moving the central tube is so great that some contrivance of the kind is necessary. At first I merely had some cotton-wool at the bottom of the tube, and fished for the little balls with an india-rubber tube let down through one window opening. On sucking air through the end with the mouth, the balls could generally be picked up and drawn out attached to the lower end of the pipe. My present plan is less precarious. W is a piece of wood loosely fitting the tube. On this there is half an inch or so of cotton-wool on which is a disc
of wash-leather just fitting the tube. A piece of thread long enough to reach beyond the window is fastened at one end to the piece of wood and at the other end to a small fragment of iron wire. The thread and wire rest upon the wash-leather, and to make sure of this a second cylinder of wood is let down to press all in place. In case of accident to the little balls, a magnetized tuning-fork is let down the tubes by a piece of string, and the iron wire pulled up. It is then easy, by pulling the thread, to bring the wash-leather to the window level and so to pick out the little balls with forceps.

Fig. 15 is a vertical section of the innermost of the series of screens employed to protect the apparatus from variations of temperature. I could not at first believe that these would be required, but each additional protection of the kind has certainly improved the constancy of behaviour of the apparatus, and I have now no doubt as to the necessity for their use. \( t_1 \) is a brass tube with inner and outer ledges split into two halves, so as to fit on to the upper part of the window casting shown in chain lines; \( t_2 \) is a plain brass tube reaching nearly to the top of the central tube, and \( t_3 \) is a third brass tube, with an internal ledge resting on \( t_1 \). This is large enough to clear the milled heads \( h_1, h_2 \). An opening is made in it large enough to allow the telescope \( T \) and all parts of the scale \( S \) to be seen from all parts of the mirror. There is also a small hole in the back, through which the tube of the window, fig. 12, can be screwed. The screen tube \( t_3 \) is just clear of the lid and the window tube.

To protect the whole instrument from variations in temperature it is completely surrounded by the octagon house, of which a horizontal section is shown in fig. 22. It is double-walled, and is made in two halves of \( \frac{3}{4} \)-inch pine boards, separated by a space of 1 inch. This is filled with cotton-wool. The top is flat, double, and packed with cotton-wool in the same way. The two halves slide together upon the table on which the instrument is placed, and meet, completely enclosing it, with the exception of a small hole in the centre of the top, through which a cord, the use of which will be described later, can pass; of a narrow slit in the front, through which the scale and telescope may be seen from the mirror; and of two small apertures through one of which the vernier \( V \) may be seen by the aid of the small telescope \( t \) (figs. 18, 19), the other admitting of the driving wheel \( D \) and air tube. The connecting wire between \( D \) and the wheelwork above lies in the narrow space between the inner and outer boards and the two styles which separate them.

By way of illustrating the state of steadiness to which I have reduced the air in the central tube, I may give the result of a calculation made in the case of Experiment 8. In that experiment the points of rest would have been disturbed by one unit if the air in the tube had been moving round at the rate of one turn in six weeks, i.e., at such a rate as to blow past the balls at a rate of 1 inch in \( 13\frac{1}{2} \) days. This follows immediately from the torsional rigidity, decrement, period, and angular value of one division. No uncertainty so great as this appears in the mean deflections obtained during the night.
The Laboratory and Accessories (Plate 2).

The apparatus is set up in the vaults under the Clarendon Laboratory at Oxford, to fit which, in fact, it was specially designed. I cannot sufficiently express my obligation to Professor Clifton for giving up to me entirely for four years this very perfect observing room, for not only was I able to make my observations under specially favourable conditions, but I have had the advantage of having at hand the resources of his splendidly equipped laboratories, and of being allowed to make any use of them that I desired. I feel that Professor Clifton's kindness in the matter is the greater as I have no claim upon him whatever, and I can only hope that in so far as my work carried out in his rooms may represent progress in practical physics, he may feel justified in having sacrificed to this end his best observing quarters.

The vault is a double one, of which the southern half is shown in plan in fig. 18. This is separated from the northern half by two piers. The entrance is by a door at the east end of the northern half. The two tables, $A_1$, $A_2$, which Professor Clifton had built for the purpose of the experiment in the positions shown, are of his standard pattern. The top, made of one slab of slate, rests on a large block of freestone, and this is supported by three walls of brick set in cement, forming an H. The instrument surrounded by the octagon house is placed upon the table $A_1$. On the table $A_2$ is arranged a large astronomical telescope $T$, by Cooke, of York, by means of which the scale is read by reflection from the mirror. The great focal length and the perfection of the object glass are necessary to obtain sufficient magnifying power to be able to read with certainty to $\frac{1}{300}$ inch on the scale; the large diameter of 4 inches has the advantage of giving a large field of view, which is almost essential in taking rapid transits. Moreover, telescopes of the same perfection of construction and length are not immediately obtainable of smaller diameter. This telescope is supported by two cast-iron standards, each with its own travelling $V$, of my own construction, which give absolute steadiness, being geometrically designed. In this way a considerable range of height can be obtained in case it is wanted. The small telescope $t$, for reading the vernier $V$, by which the angular position of the lid and of the large balls $M M$ is determined, also stands on the table $A_2$. Besides the telescopes, a pulley-wheel $p_1$ rests upon the table, and a driving-wheel $d$ is clamped to it; $p_1$ is pulled by a stretching weight, so as to keep the blind cord $b$ passing round the other wheels $p_2$, $p_3$, and fastened to the go-cart $g$ in a state of tension. The cart is a beautifully executed specimen of part of a "natural philosophy set" of the last century, and was lent me by Mr. G. S. Newth. It runs on the wooden framework, which is wedged into the recess at the east end of the room, between a pair of rails made of angle brass. It carries an albo-carbon lamp, so that the flame can be brought behind any division of the great scale $S$, which may be seen in the telescope $T$ by reflection from the mirror. The flame is turned down very low to avoid heating the room unnecessarily. I
generally set it so that the flame is about \( \frac{1}{4} \) inch wide and \( \frac{1}{8} \) inch high. The driving-wheel D is made with two heavy projections not shown in the figure, to give it considerable moment of inertia, and with the handle at a distance of an inch about from the axis. Any motion given to it by hand is therefore less likely to be subject to jerks than it would be if unweighted. A very light cord rests loosely round this pulley, is supported by an arm of wood projecting from the other end of the table, is supported again on the edge of the other table, and then lightly passes round the little wheel D, figs. 1 and 2. This rests upon the table, and is kept from moving about by a weighted foot. Two pins fastened into the wheel D engage in a hole and slot in the cross-piece \( y \) at the bottom of the hanging wire \( b \). Thus when D is turned the motion is communicated to the wheel-work WWW through the light and loose cord, the wheel D, and the cross-arm and wire. The only kind of force between the wheel D and the wire is by the construction a couple, and this, owing to the high ratio of gearing in the wheel-work WWW, need be only very small to give motion to the lid L. The friction due to the great weight of the balls MM, and of the lid, is largely reduced by hooking to the two rods RR screwed into the lid guys joined to a cross-bar above the bell-jar, which there hangs from a single line passing round the centre one of five wheels secured to the arch, the edge of this being exactly above the axis of the instrument. The line then passes over a second wheel close to the west wall of the vault, and carries two weights each exactly equal to one of the balls, and an extra weight to partly balance the weight of the lid. When the handle of the wheel \( d \) is turned the lid slowly and almost insensibly creeps round, and no tremor appreciable with ordinary apparatus is communicated to the suspended mirror. Owing to the extreme sensitiveness of the apparatus, and the very great magnifying power, a high period tremor is set up in the mirror, about equal in amount to that caused by ordinary traffic in St. Giles', about a quarter of a mile away. This dies away very rapidly, and I am unable to trace any anomaly to this cause. The corner of the vault, in which the instrument is placed, is screened off from such small variations in temperature as my presence and the small gas flame produce, by two double partitions of felt, \( f_1 f_1, f_2 f_2 \). Furthermore, the vault itself is protected from variations in the temperature of the air, in the long underground passage by which it is approached, by two felt curtains some distance apart.

Slits and holes, no larger than are necessary, are made in the partitions \( f_1 f_1 \) to allow the scale and telescope \( T \) to be seen from the mirror, the vernier \( V \) to be seen from the telescope \( t \) and the light string to pass through. These partitions are temporarily lifted out of the way when a certain beam \( l_1 \), shown in position in fig. 19 but not in fig. 18, is being used. The two beams \( l_1, l_2 \) have their upper edges planed true, and are so supported by levelling screws that their upper edges form one level straight edge. These are employed when the distance from the scale to the mirror is being determined in the manner to be described under the heading "The Steel Tape and Accessories." The beam \( l_2 \) I leave in position permanently, but as \( l_1 \) would be in the way, it is only put up when required.
The Large Scale.

The large scale is etched on a piece of plate-glass 9 feet long, 6 inches wide, and half an inch thick. The divisions are 50ths of an inch, and there are 4800 of them. I made many experiments to find the most suitable kind of scale and thickness of line to suit the mirror which I had to use. I shall return to this point when I explain the advantages that I have gained by the use of the curious form of beam mirror. It is sufficient to state now that the divisions are black upon a clear ground, and that the thickness of the lines is greater than at first anyone would be likely to think suitable, being about $\frac{1}{250}$ of an inch. The method by which the scale is held rigidly and definitely in place but without strain, is illustrated by the isometrical projection in fig. 23, which shows one end only. ZZ are a pair of gun-metal castings screwed to the wood frame which is securely wedged into the recess at the east end of the vault. u is a brass rod passing through a hole in each casting and able to be clamped by a screw at each end. v is a casting with a cylindrical piece turned at each end and exactly the same length between shoulders as u is. This rests at each end upon a levelling screw, and can be clamped by pinching screws. At the other end of the scale, 9 feet away, there is an identical construction. Two plates of glass, the back one of which is a dummy, the front one only being divided, rest upon the cylindrical projections of v, being definitely held in position by the V notch shown, which of course is only at one end. The glass plates rest also against the shoulders and against the ends of u v and are kept in contact by the action of a bent piece of brass at each end which lightly presses them towards one another. The glass plates are therefore geometrically clamped, each resting on seven points, the one in excess of six being introduced to counteract the one degree of freedom which the flexure of so long a plate introduces. The middle of the front plate is silvered at the back up to near the line of divisions, which is 1$\frac{1}{2}$ inch from and parallel to the upper edge. The levelling screws enable me to bring the upper edge and therefore the line of divisions truly level, and this is finally tested by observation with the telescope and swinging mirror. The rods u and v are then gently worked in or out as needful until an observer with his eye at the window of the apparatus in the place of the mirror sees the window reflected from the clear glass on the line of divisions. The silvering of the middle of the scale is not absolutely necessary, but it enables one more quickly to recognize the position of objects placed against the lower part of the apparatus and so acts as a finder. When the scale is thus adjusted and has been placed with its divisions on a level with the mirror, a division not far from the middle will be the point at which a perpendicular dropped from the centre of the instrument will cut the scale. The eight pinching screws are then clamped and this division is recorded when its position has been more accurately determined by the use of a small telescope in the place of the eye. The division 2260 was the perpendicular reading.
in all the experiments made up to the present. The dummy was provided partly to absorb radiation from the flame and so to protect the working scale from heating, but mainly so that I should have a glass plate ready to divide myself without loss of time in case of accident to the working scale. This happily has not occurred.

I calibrated this scale by reference to an American steel scale divided into 50ths of an inch, the uniformity of which I had previously tested. This steel scale became for the purpose of the angular measurements the standard to which everything was referred. For this purpose its absolute value is of no consequence; all that matters is its uniformity. A long board was supported so that its upper surface was everywhere level. Sheet lead strips were rolled until they were just thicker than the steel scale and a double row were laid upon the level board. The glass scale was made to rest upon these with its face downwards and the steel scale was slipped underneath, so that the glass and steel divisions should be superposed. An erecting eyepiece was placed on a stand above the glass and was used as a reading microscope. Every tenth division was observed, and the 480 corrections were entered in a book, and were also plotted out on an enlarged scale, so that an error of \( \frac{1}{100} \) inch should be represented by \( \frac{1}{10} \) inch. From the irregular curve drawn through all the points the calibration error of every scale reading was afterwards ascertained. In order to determine the circular error, the true distance in scale divisions between the mirror and the scale was measured according to the plan to be described on p. 17. A large number of values of the circular correction were calculated from the expansion for \( \tan^{-1} x \) and tabulated in terms of scale divisions. It was necessary to include the term \( + \frac{x^2}{3} \) as at the ends of the scale this amounted to half a division, while at 1800 divisions on either side of the perpendicular reading it was one-tenth of a division. The perpendicular reading 22,600 being invariable, these corrections were plotted on the same sheet as the calibration errors, thus the two corrections could be taken out simultaneously for every reading which was thus converted into the reading that would have been obtained if every division subtended the same angle at the mirror. In this way the time and labour that are ordinarily required in finding the angles corresponding to scale divisions and in correcting for calibration are reduced to a few seconds for each, and error is almost impossible.

The Overhead Pulleys.

The overhead wheels are eight in number, and are all of the same size. Five are over the instrument, and three close to the west wall. As already stated the edge of the middle one, which has a round groove in it, is exactly over the centre of the apparatus. Those on either side have flat-bottomed grooves, and they can be placed either 6 or 4 inches apart, according as \( 4\frac{1}{2} \) or \( 2\frac{1}{2} \)-inch balls are to be used. Outside these, and the same distance apart as the screwed pillars R R in the lid, are two round
grooved wheels. The central wheel of the set near the west wall is round grooved, and the other two, which can be set either 6 or 4 inches apart, have flat-bottomed grooves. The purposes which these wheels serve are numerous and important. In the first place the middle ones are employed to reduce the friction of the lid, as has already been explained. In one of the cathetometer operations the lead balls and the tops of their supporting pieces have to be observed in order to find the levels of their centres when they are hanging out of sight inside the apparatus. At the same time the lid must be raised, and held out of the way; but it cannot conveniently be removed altogether. To accomplish this, steel bands are passed over the flat-grooved pulleys, and are each of them pinned to the ball holder at one end and hooked to an exactly equal counter-weight at the other. The balls can then be raised, and will remain hanging at any level at which they may be left. Two cords are hooked on to the eyes of the pillars R R of the lid, and after passing round the outermost pulleys above, converge, and then, becoming single, pass over the central pulley next the west wall. There, a weight exactly equal to the lid, serves to counterbalance it, so that it will remain suspended in a horizontal position at any level. The height is so chosen that one of the ball holders is just above the pillar on its side, while the other is just below the lid on the other. The balls are then at the same level, and their upper portions can be seen just above the edge of the casting C. The balls under these conditions hang quite freely, neither touching the instrument nor being deflected by contact between their wires or steel bands with the lid. The steel is necessary to give definiteness to the positions of the lead balls during the cathetometer measures as if they were to hang from cord the twisting and uncertain and variable stretching would make accurate measurement impossible. The central overhead wheel alone is employed in placing the small balls in position. I used at first, after fixing them to their own fibres and hooks, and measuring the distances when hanging from the point of the hooks to the tops and bottoms of the balls, to get them in through the window, supporting the hook by a bent pin held in one hand and passing the fibre over a bent pin held in the other. The process was one of great delicacy and difficulty, but it answered with gold balls 2 inch in diameter. It was, however, next to impossible with balls of double the weight, as the fibre would not, under such a strain, bend round a pin, a polished steel rod, or anything that I could think of. I had therefore to adopt the plan with the overhead wheel, which has never failed. A pin, with the point bent at right angles to form a horizontal hook, is tied to a piece of sewing silk, and allowed to hang from the central pulley. A weight equal to the ball is tied to the other end. The pin-hook is inserted in the eye of one of the hooks and eyes from which the gold ball is suspended, and pulled up till the ball is over the tube. It is then let down until the eye is opposite the window, when its hook is made to rest upon the point of a large pin held in one hand; by this means it is transferred to the side hook where it is left hanging by its eye, and ready to be placed upon the arm of the mirror when that is in position.
The Steel Tape and its Accessories.

In order to make an accurate determination of the optical distance between the reflecting surface of the mirror and the foot of the perpendicular upon the scale, I have prepared a steel tape to lie upon the beams \( L_1 \) and \( L_2 \) already described, and two sliders, one carrying an erecting eyepiece or low power microscope, and the other a sliding brass rod.

The steel tape is one of ordinary construction, half an inch wide, and divided on one side in millims. and on the other in inches and eighths. As the lines on this, as is necessary with etched tapes, are thick and raised above the general surface, I engraved fine lines on the divisions—2 inch; 7 ft. 4 in.; 14 ft. 6 in.; 21 ft. 8 in.; and 21 ft. 9 in. After removing the lead slips which had supported the glass scale while it was being calibrated, I laid this scale face downwards on the steel tape, setting 0 of the glass scale upon the first engraved line at 2 inch. The reading in scale divisions of the fine line at 7 ft. 4 in. was then observed to be 4302.5. The tape was drawn back until 0 of the glass scale was over 7 ft. 4 in., and the reading taken for 14 ft. 6 in.; this was 4302.85. The readings for 21 ft. 8 in. and 21 ft. 9 in., taken in the same manner, were 4302.5 and 4352.5. The temperature was 19°-75 C. The calibration correction for the division 4302 of the glass scale is 3°. Hence the distance in corrected scale divisions from the engraved lines at 2 inch and 21 ft. 8 in. at 19°-75 C. is 12898.85. The glass scale was calibrated in terms of the steel standard at 14°-5 C.; it had, therefore, relatively contracted at the higher temperature. Taking 0.00002 as the differential coefficient of expansion, the distance between the engraved line becomes 12898.98 in terms of the divisions of the standard steel scale at any temperature. The sliders have bases made of plate glass, on each of which is an engraved cross line. One carries on two V's the low power microscope, and this, after the tape is placed in position, is arranged with its cross-line over the engraved line on the 2 inch division. The microscope is then made to slide in its V's until a small cross engraved at the centre of the back of the freely suspended mirror is seen through the front window sharply in focus. The microscope is then clamped to its V's, and the slides moved out of position and again set several times, the relative position of the engraved lines being noted. If these are systematically on one side, the microscope is shifted in its V's until repeated settings bring the engraved lines together. At the other end of the tape a corresponding slider is placed with its engraved cross-line over one of the engraved lines at 21 ft. 8 in. or 21 ft. 9 in., and the brass rod is slid forward until it just touches the scale at the foot of the perpendicular from the mirror. The two sliders are then placed upon the original steel scale, from which the glass scale was calibrated, and moved until the fine lines on the end of the brass rod are seen sharply in focus. The distance between the engraved lines on the plate-glass bases, so determined, added to the distance between the engraved lines at 2 inch and 21 ft. 8 in. or 9 in., as the case may be, is MDCCCXCV.—A.
the true optical distance from the reflecting surface of the mirror to the foot of the perpendicular upon the scale. This includes the small correction for the reduction in distance owing to the refractive power of the glass composing the mirror and front window. The divisions on the scale are, of course, placed on the side facing the instrument, so that no refractive correction is needed for the scale.

The Optical Compass.

In order to make the horizontal measures of the distances between the wires from which MM hang, and the quartz fibres which carry mm, measures which have to be made with the greatest possible accuracy, I had to design a special instrument which was suggested to me by Professor Clifton’s optical compass. That is an arrangement by which two microscopes can be made to slide parallel to one another. After being simultaneously focussed on the two marks whose distance asunder is required, the frame to which they are clamped is rotated so as to bring them relatively unchanged in position to view a scale divided by lines microscopically fine. In this way the distance is directly transferred to a scale in terms of which it is known. In my case the chief difficulty was to keep the whole apparatus confined within the horizontal limit of 1½ inches, which was all I had liked to allow myself in the design of the apparatus itself. Into this space I had to get (1) a rotating slide to move on the lid round the axis of the apparatus; (2) a focussing slide to move to and from the plane of the wires and fibres; (3) a pair of traversing slides, each to carry one microscope capable of being separated by a fine adjustment and with a motion parallel to the planes of the fibres and wires. It was essential, moreover, that the slides should be very rigid, and that the focussing slide in its traverse should remain upon the same supports to avoid difference in flexure in case there should be any. The geometrical principle was of course followed, each moving piece resting on five independent small surfaces, and free from mechanical constraint. This instrument is shown in figs. 24 to 29. To avoid confusion, the rotating and focussing slides, with scale and micrometer screw only, are shown in figs. 24, 25, 26, in full lines upon the lid in chain lines, and the focussing and traversing slides in figs. 27, 28, 29. The rotating slide R rests upon the lid by means of two curved V’s, ν1ν2, resting in a circular V groove upon the lid, and by the flat surface f bridging the V groove at the back. It can, therefore, rotate upon the lid without shake, but no other motion is possible. This piece is made very stiff by the raised rib r round the triangular part, and by the overhanging ledge which extends over its whole width. The rotating slide also carries a micrometer screw S of 100 threads to the inch, with a head divided into 100 parts, and two parallelizing screws, S1S2. On the flat surface before S2S3 a glass microscopically divided scale stands upon two little glass feet. Full particulars of this will be given after the description of the optical compass. It merely rests against the parallelizing screws and can be moved bodily to the right by the micrometer screw. No slide of any sort
is provided, this simple construction, though perhaps less convenient, being far more perfect than any possible kind of slide.

The focussing slide $F$ rests upon $R$ by means of the two $V$'s, $v_2v_3$, which fit into a straight $V$ groove in $R$, and by means of the flat surface $f_2$, which rests upon a planed surface parallel to the $v$ groove. This focussing slide is stiffened by longitudinal ribs above and below the general level, one on one edge, and the other on the other edge. It also carries a focussing screw $S_4$ of 50 threads to the inch roughly divided on the head. This merely pushes against the tail rib of $R$, causing the slide $F$ to retreat from the centre of the apparatus. It can be moved the other way by hand, or by a gentle forward pressure on the screw head when it is being turned backwards. As it is necessary to be able to give a fine focussing movement to this slide in two separate positions, about one inch apart, a focussing block $b$ of the required length is pivoted on $R$, so that it may either remain out of use as shown in the figures, or may be brought under the focussing screw after the focussing slide has been withdrawn. A turn or two is all that is necessary then for the purpose of focussing in either position.

Two traversing slides $T_1$, $T_2$ each rest upon the focussing slide by five small surfaces, of which four in each case are due to the long projecting $V$'s $v_3$ on the front edge, of which the middle parts are scraped so as not to bear upon the longitudinal $V$ groove in the traversing slide.

The fifth point in each is formed by a small friction wheel $w$, which lies in a recess in the traversing slide, and runs upon a planed surface on $T$ parallel to its $V$ groove. The reason that I introduced a wheel here is, that while a very small vertical uncertainty is of no consequence, I was thus able to cause the whole of the frictional resistance to traversing to lie in the $V$ itself, which is the more necessary as the distance between the ends of the $V$ is necessarily less than the distance perpendicular to it. This is taken advantage of further, for I have arranged that the force that draws the two traversing slides together is produced by a long, very small helical spring of steel lying in a hole drilled in the $V$'s themselves, thus being in the line of friction and producing no tendency in either to depart from its geometrical bearings. For the same reason I have made the fine adjusting screw which separates them act in the same line. This consists of a fine steel screw $S_5$, fitting rather loosely in its very short nut, carried by $T_2$ at one end, and with a fine polished conical point at the other, which rests between a little $V$ carried by $T_3$ and a vertical surface on $T_1$. The screw and cone piece, therefore, are free from constraint, but simply push the traversing slides apart in the same line where the friction and the opposition of the spring act. Thus, when the screw is turned forwards, the slides simply separate to a minute extent, but have no tendency to lose their parallelism. Each traversing slide is furnished with three grooves cut away so as to support a microscope lying in any of them at each end only over small surfaces at 45° on either side, thus allowing it two movements, one of rotation, and one fore and aft. The latter is prevented by
the use of focussing collars C, C, which slide stiffly on the microscopes and are so adjusted that when the two microscopes are alternately placed in the same groove and pushed up to their focussing collars they will each be in focus upon the same object. The positions of the grooves are such that the microscopes, when in their symmetrical positions, can be brought upon points distant from one another by 1, 4, or 6 inches, with a small margin on either side of a few hundredths allowed by the screw cone. Each microscope is furnished with a cross-wire and an eyepiece divided scale, one or other of which can be used according to the position of the positive eyepiece. If the microscopes are laid in grooves that do not correspond with one another, they may also be focussed upon points 2\(\frac{1}{2}\), 3\(\frac{1}{2}\), and 5 inches apart. If the two traversing slides are made to exchange places, for which purpose the screw cone has an extra nut and bearings provided, then distances of 2, 3, and 4\(\frac{1}{2}\) inches can be measured also, should any of them be required.

Beyond stating now that the optical compass does a great deal more in the investigation than merely measure horizontal distances between vertical wires or fibres, and that the geometrical and rigid construction makes it possible to work to the full limit which optical definition imposes, I shall not at present explain the details and the order of the operations carried out by its aid. They will come more conveniently under the description of the experiment itself (Operation 9, p. 40).

The Small Glass Scale.

This was made for the optical compass by Zeiss. A strip of plate glass 6\(\frac{1}{2}\) \(\times\) 1 \(\times\) 1\(\frac{1}{4}\) inch was divided by lines microscopically fine as follows. A line was ruled at every inch from 0 to 6, and at 2·50 and at 3·50 inches. In addition to these, five lines, \(\frac{1}{2}\) of an inch apart, were ruled on either side of the divisions 1·00, 2·50, 3·00, 3·50, 5·00, and 6·00. The five on either side of the zero were by inadvertence omitted, and the zero line was, by some obscure accident, ruled at 0·04 instead of at its true place. This, however, was of no consequence, as the 6-inch distance was measured by reference to the divisions 0·04 and 6·03, 6·04, or 6·05. The 4-inch distance (not yet wanted, however), by reference to 1·00 and 5·00, and one or two contiguous divisions, and the small distance which was to have been 1 inch about, but which is in reality almost exactly 1\(\frac{1}{2}\) inch by reference to 2·55 and 3·45. When I was in Cardiff at the meeting of the British Association, Professor Viriamu Jones allowed me to measure the absolute distances between these divisions and a few on either side upon his measuring machine. This machine is one of Whitworth's tenthousandth machines, but of more than usual stability, and with a bed long enough to take in bars three feet long. It is provided with a set of these bars increasing by inches from 1 to 12 inches, and with a 2-foot and a 3-foot bar. The glass scale was attached to the upper surface of the tail headstock by being simply pressed down edgeways upon two wafers of soft wax, and it was pressed endways against a third
on the index. Safety fingers of wire were also attached to the headstock, but not in contact with the scale, so as to prevent it from falling, if it should by accident get displaced. One of the microscopes of the optical compass was allowed to rest in brass V's bolted to a solid iron casting, which rested on the same slate-topped pier as the machine. The microscope was moved in its V's until one end of the scale was in focus; the tail headstock was then traversed on the bed of the machine until the other end was opposite the microscope. The scale was then moved until this end was in focus, but the process, being only carried out by the fingers, was difficult to perform, as besides fixing the scale parallel to the bed as tested by the focus of the microscope, it was necessary also to see that it remained parallel in the vertical plane, and to adjust this by pressing out or adding to the soft wax wafers by which the scale was lightly held. At first this quadruple adjustment, in which the setting of one right generally put the other three out, seemed as if it would require for its successful accomplishment some mechanical contrivance more under control than the fingers. However, by a happy accident, I succeeded in soon getting the scale so that I could detect no want of parallelism either way with the fairly powerful microscope that I was using. The actual distances were determined along a line about \( \frac{1}{60} \) of an inch below the upper ends of the short divisions.

The distances which it was necessary to know with the greatest accuracy, were those from 0 to 6, from 1 to 5, and from \( 2\frac{1}{2} \) to \( 3\frac{1}{2} \). These were determined as follows. The loose headstock was traversed on the bed, and clamped when the division at one end of the distance to be measured was on the cross-wire of the microscope. A bar was then put in, the feeling piece put in its place, and the micrometer head turned until the feeling piece was just prevented from slipping, when the reading was taken. The headstock was unclamped, moved, and the process repeated until two or three readings had been taken. The bar was then removed, the loose headstock moved until the division at the other end was on the cross-wire, and a new bar of suitable length put in, and the micrometer turned until the feeling piece was again just held. When the three readings had been taken in the second position, the headstock was set back to the first position, the first bar placed in position again, and three new readings taken; then in the same way three more were taken in the second position. The microscope was not touched at all during the process.

In connection with these measures, the following important details may be referred to. I found great difficulty in setting the loose headstock by means of the high-pitched leading screw, especially as the wheel was almost out of reach, and in seeing the cross-wire in the eyepiece projected upon any division of the scale so as to bisect that division exactly. These difficulties were practically removed by placing the microscope so that its cross-wire was slightly inclined to the vertical in which direction the divisions are ruled, and by setting the ruled lines symmetrically between a pair of microscopically fine specks of dust upon the cross-wire which, with the particular inclination then, just lay on either edge of the line. The width of the line
itself was found to be \( \frac{1}{30000} \) inch. In this way there was no doubt as to the setting of the cross-wire accurately to a tenth of the thickness of the line. I was not, however, always able, owing to the circumstances to which I have already referred, to leave the headstock set and clamped so accurately in position, that I could detect no want of symmetry in the microscope. In a few cases I left it with a + or - error of one-tenth of a division as estimated by the eye, which error I entered in the notebook at the time, and before I knew what the reading of the Whitworth machine would be. These were taken by Mr. Harrison, the very skilful assistant in the Physical Laboratory at Cardiff, and he did not know what correction I had entered, or indeed, if I had entered any correction. His reading was then entered into the book also. In this way I hoped to avoid that spurious appearance of accuracy that is apt to result from knowing during a process of adjustment when the last setting has been reproduced. The temperature, of course, was frequently taken, but it only rose half a degree during the day, and to avoid as far as possible differences in temperature in the apparatus, the bars that were used were kept during the measurements upon the bed of the machine. As an example, I give the figures of the middle inch exactly as they were entered. The whole numbers represent \( \frac{1}{100000} \)ths, and the decimals \( \frac{1}{1000000} \)ths of an inch.

<table>
<thead>
<tr>
<th>Division on Scale</th>
<th>Bar used.</th>
<th>Reading and correction.</th>
<th>Reading and correction.</th>
<th>Reading and correction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\frac{1}{2} )</td>
<td>9-inch</td>
<td>[ 315.1 ] [-.2 ]</td>
<td>314.9</td>
<td>315.0</td>
</tr>
<tr>
<td>( 3\frac{1}{2} )</td>
<td>8-inch</td>
<td>313.3</td>
<td>313.4</td>
<td>313.6</td>
</tr>
<tr>
<td>( 2\frac{3}{4} )</td>
<td>9-inch</td>
<td>314.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3\frac{3}{4} )</td>
<td>8-inch</td>
<td>312.9</td>
<td>[-.2 ]</td>
<td>312.8</td>
</tr>
</tbody>
</table>

Temperature 16°-9 C.

The distance between \( 2\frac{1}{2} \) and \( 3\frac{3}{4} \) on the scale found by taking the simple mean of the above figures and subtracting, is \( .99983 \) inch, or allowing for the gradual change, due probably to temperature variation, which seems to have been going on at this part of the day (about 1 p.m.) more particularly, the distance is \( .99986 \).

A determination, made early in the afternoon, of the same distance by direct comparison with the 1-inch bar, the 8-inch bar remaining in the machine, gave as the length of the middle inch of the scale \( .99979 \). Since the bars are not guaranteed to be nearer to the truth than \( \frac{1}{100000} \)th of an inch, the agreement between the 1-inch bar and the difference between the 8- and the 9-inch bars is better than might have been expected. Meanwhile, I may consider for the present that the true length of the middle inch is known with an accuracy of 1 in 10,000 at least. I have taken it to be equal to \( .99980 \).
The interval 1:00 to 5:00 was compared with the difference between an 11-inch and a 7-inch Whitworth standard bar. Assuming the difference to be 4 inches, this interval was found to be 3.99970 inches. In the same manner the interval between zero (really 0.4) and 6:00 was found by comparison with the difference between a 12-inch and 6-inch Whitworth standard bar to be 5.95996 inches.

The distance from 6:00 to each of the divisions up to 6:05 was measured in the Whitworth machine, and also by means of the micrometer screw of the optical compass. The value of the screw was found in terms of the middle inch of the scale, which had been measured most carefully upon the Whitworth machine. The screw measures were found short by .145 per cent. Allowing for this the distances were found to be:

<table>
<thead>
<tr>
<th>Between</th>
<th>By screw corrected</th>
<th>Total from 6:00</th>
<th>Corresponding totals measured in Whitworth machine</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:00 and 6:01</td>
<td>.010145</td>
<td>.010145</td>
<td>.01015</td>
</tr>
<tr>
<td>6:01 to 6:02</td>
<td>.010105</td>
<td>.020250</td>
<td>.02019</td>
</tr>
<tr>
<td>6:02 to 6:03</td>
<td>.009815</td>
<td>.030065</td>
<td>.03002</td>
</tr>
<tr>
<td>6:03 to 6:04</td>
<td>.009915</td>
<td>.039980</td>
<td>.03995</td>
</tr>
<tr>
<td>6:04 to 6:05</td>
<td>.010085</td>
<td>.050075</td>
<td>.05012</td>
</tr>
</tbody>
</table>

Adding the measures of the intervals '01 to 6:00, and 6:00 to 6:04, the sum is 5.99994 or 5.99991 according to the value taken for the smaller interval. Mr. Chaney allowed me to measure the distance from '04 to 6:04, at the Standards Office, by comparison with the intervals 24 to 30 and 30 to 36 in the standard yard measure. The two measures did not differ by an amount that could be detected and the result was found to be 5.99995 at the temperature 59.7 F. There was no question, therefore, that the 6-inch distance was known correctly to one part in 100,000.

The distances from 2:50 to 2:55 and from 3:45 to 3:50 were measured by the micrometer screw of the optical compass, and their sum was found to be (employing the corrected value of the screw) 100125, so that the distance between the divisions 2:55 and 3:45, which are those actually used in all the measures of the horizontal distances between the fibres, is 89967. There can be little doubt that this is correct to one part in 10,000 and, as a small error in the working length of the beam produces an error of about the same magnitude in the result, the value of G is not likely to be affected seriously by uncertainty in the value of this inch. I did not attempt to determine this inch at the Standards Office, as I found that, owing to the coarseness of the lines on the standard bars and the imperfect optical means, so small a distance could not be measured with a high degree of proportionate accuracy. Should the rest of the experiment ever be carried out with such perfection that a possible doubt of one in 10,000 on this measure becomes of importance (and I see no reason why it should not), then I should have to rely upon a measurement made at the International Bureau at
Sèvres, but up to the present I am quite content with that made upon the Whitworth machine.

The Clock.

The clock, the position of which is indicated in fig. 18, is a Frodsham regulator, which was lent to me by the late Professor Pritchard, who took a great interest in the experiment. The present owner has kindly allowed me to retain it until the work is finished. The clock is placed so that it can be seen from the observing stool at the telescope, and is illuminated when necessary by a small incandescent lamp. It is employed to mark time upon a smoked drum, upon which also are marks made by the action of a key at the telescope. I finally determined to employ the chronographic method after seeing Professor Cornu’s apparatus. To the lower end of the pendulum I screwed a platinum wire flattened and filed to a rounded edge at its end, the edge being in the plane of oscillation. This passes through a horizontal line of mercury, standing up by its capillarity above a transverse groove in a piece of wood. The end of the groove opens into a large well filled with mercury, so as to retain the purity and the level. The wood on either side of the groove is cut away to an edge, so that mercury dust carried over by the platinum cannot accumulate and give trouble. The wood is so placed that when the pendulum is moving through a small swing of a quarter of an inch only, the time marker actuated by the contact ticks regularly. With the full excursion the alternate marked seconds are then indistinguishable in length. I soldered two platinum wires to the second hand and brought an insulated elastic platinum point over the seconds dial and under the minute hand, so that the second hand should make contact twice a minute. I so bent the wires that at the minute contact should be made again immediately after the pendulum had broken contact, and retained till the end of the first second, while at the half-minute it was made again after the thirtieth second and immediately broken. The minutes and the half-minutes were in this way clearly and differently marked (fig. C, p. 48), and it was thus unnecessary to count more than 15 seconds on the charts. The time markers and the drum to carry the smoked paper were made by the Cambridge Scientific Instrument Company, and are of their well-known pattern. I took out the long heavy wires of the time markers, which, I understand, are made to the order of the physiologists, and replaced them by very small and light styles of copper foil tapering to a point. The two are arranged close together so that the tracing points are not more than $\frac{1}{100}$ of an inch apart. The sheets of paper, 12 × 19 inches, are most readily smoked when stretched on the drum by pouring a little benzine into the india-rubber pipe which supplies a fishtail burner. The very smoky gas flame which results rapidly produces a deep and uniform coat of soot. The sheets when finished are passed through a bath of very dilute shellac varnish, the strength being such that the smoke does not rub off, but may have numbers, &c., readily scratched upon it with a pointed style. The drum is driven through worm
gearing by a P1 electric motor, by Cuttriss, of Leeds, the current being supplied by a couple of E.P.S. cells. Mr. F. J. Smith has kindly allowed me to charge them when required at his laboratory. The same cells are connected up to the two time-marking circuits, and to a small electric lamp placed in the octagon house to illuminate the vernier and divisions close by. This is lighted by raising, and so making the upper contact of the key, which on depression is employed to make the signal marks from the telescope. Owing to the self-indication of the small electromagnet of the time marker, a considerable spark would be formed at the mercury break in the clock, to the destruction of the contact, if it were not for two electrolytic cells in series, charged with battery acid and with platinum electrodes, which are employed as a bridge across the clock break. This sets up an electromotive force of polarization which prevents any current from passing when the contact is kept broken, but its resistance is so small that the high electromotive force set up at the break is able readily to fall through them, thus practically abolishing the spark. I found this greatly superior in every way to a non-inductive resistance. There is one point connected with this break which I believe to be worth recording. To ensure good contact I amalgamated the platinum point with sodium amalgam, but immediately found that the contact lasted longer, and was more irregular than before. However, I left the point amalgamated for a fortnight, during which it gave more trouble by drawing the mercury out of the trough. I then unamalgamated it by holding it over a candle flame, until I concluded that the mercury was all gone. I did not make it very hot. Since that time the contact has never failed, which it occasionally used to do before. I attribute the improvement to an atomic roughening produced by the penetration of the mercury. Before the point was unamalgamated, the pendulum, as I afterwards discovered, made a second contact with a pool of mercury drawn out of the trough and electrically insulated, which contact mechanically disturbed its period. For this reason Experiment 4 is incomplete, as its time observations are untrustworthy. I took, however, the rigidity of the fibre from Experiment 5, and so completed the calculation.

The Large Balls and their Supports.

One of the difficulties in the preparation of apparatus for measuring the mutual gravitation of comparatively small bodies is met with in making the large balls. Cavendish employed large balls of cast lead 1 foot in diameter. Professor Poynting made the balls in his apparatus of an alloy of lead and antimony, for the sake of the extra hardness, which would make it easier to turn them accurately to form and would render them less liable to subsequent deformation. Though special precautions were taken to avoid cavities, and to obtain homogeneity, the large one was found to act differently in different directions, and he localized a cavity by observations in this way. Afterwards he found the centre of gravity was to one side of the...
centre by an amount corresponding very nearly with that which he had deduced from his gravitational observations. I do not feel satisfied myself that this affords any proof of the existence of an actual cavity, as a gradual variation of density, such as might easily occur in an alloy, might have produced the same effect in each case. For this reason, when a much higher degree of accuracy is being sought for, I consider that alloys are fatal to success. Professor Cornu has without any doubt avoided any uncertainty as to cavities or uniformity of density, or probably truth of form, by employing mercury aspirated from one pair of spherical hollow cast-iron moulds to another pair so placed as to reverse the attraction. By this means it seems to me everything may be known with more than abundant accuracy, except the actual position of the centres of the spheres, or what comes to the same thing, their actual distances from the centres of the attracted masses. As I explained in my first paper, in my arrangement, the difficult geometrical measurements are almost all made of secondary importance. A small uncertainty in the levels is, as in previous arrangements, of secondary importance, as in this sense they are at a position of maximum effect. A small uncertainty of the angle of azimuth does not matter, for this also is at a position of maximum effect. If there is a small eccentricity of position of the gold with respect to the lead balls, either in the plane of the lead balls, or across that plane, again the effect is infinitesimal, for the departure is from a minimum of effect in the first case, and a maximum in the second. The only measures of serious importance, on the accuracy of which the result directly depends, is the distance in plan from the centre of one lead ball to the centre of the other, and the corresponding distance in the case of the gold balls. In the first there must not be an uncertainty of \( \frac{1}{3000} \) of an inch, or in the second of \( \frac{1}{10000} \) of an inch. I do not think it would be possible on Professor Cornu's plan to obtain a knowledge of the positions of the centres of the mercury spheres, especially when one is six inches above the other, with anything like this degree of accuracy, and therefore, though with the large apparatus he used, and the proportionally lower degree of accuracy that was sufficient, the plan is most excellent, and answers perfectly, it would not be suitable in the present case. There is a second objection depending upon the magnetic quality of the iron moulds. For though to ordinary tests the beam and gold balls are not affected by magnetism, I have felt that in measurements of forces of such supreme delicacy it is safest to avoid introducing magnetic materials, lest any systematic disturbance should be introduced. I have however, satisfied myself by experiment since putting up the apparatus, that a magnetic force much greater than that due to the earth produces no effect.

The plan that I have adopted seems to me to be free from the objections that I have urged, to be easily carried out, and to be specially adapted to the purpose of exact measurement of the distance in plan from the centre of one ball to the centre of the other.

Mr. Munro, who has special experience in accurate spherical work, made the cast-iron mould shown in figs. 16 and 17. The internal hemispheres are turned out so
truly that the steel disc used as a template would audibly rattle when placed in
either alone, but could not be got in at all when a single strip of cigarette paper was
inserted on one side only. The two halves can be screwed together by means of six
steel bolts as shown. A \( \frac{1}{4} \)-inch hole is bored in the centre of one hemisphere and
one of \( \frac{3}{4} \)-inch in the centre of the other. Into the latter an accurately fitting steel
plunger was inserted, and when pressed down to the head, was turned at the inner
down, so as to complete the sphere. A small hole is drilled on the equator, enlarged
almost immediately to a greater size. Into this a brass plug can be pushed. Before
being used, the mould is warmed, and the internal surface smoked with a gas flame.
Into the \( \frac{1}{4} \)-inch hole the brass ball-holder \( e \) is inserted. A number of these were made
by Mr. Colebrook, of the utmost possible accuracy of the form shown, this being a
\( \frac{1}{4} \)-inch sphere, surmounted by a \( \frac{1}{4} \times \frac{1}{4} \)-inch cylinder with a shoulder of \( \frac{1}{4} \)-inch, of
such a depth that when pressed home the \( \frac{1}{4} \)-inch sphere should be tangential to the
\( 4 \frac{1}{4} \)-inch sphere. Though these ball-holders were made to measure only, their weights
were closely alike, being 10.70 grams for each before cutting the slot and drilling the
cross hole, and 10.28 afterwards. Since the whole effect of the gravitation of these
ball-holders and of the \( 4 \frac{1}{4} \)-inch lead balls, all in their ultimate positions, is \( \frac{3}{5} \times \frac{1}{9} \) in
excess of what it would be on the supposition that the whole mass is concentrated at
the centres of the lead balls, any doubt as to the amount of the correction, which
cannot be so much as one part in a hundred, leaves an uncertainty in the result of
about one part in a million, and is of no consequence. I should state here that this
correction includes the very small pieces of brass fastened to the lower end of the
wires, which with their pins were made to occupy the same volume as the material
removed in the slot and cross hole. The brass ball-holder, before being inserted
in the smoked mould, was tinned on the spherical surface, and then wiped to remove
superfluous metal. The mould was then put together, and the steel bolts, after being
well rubbed with blacklead, screwed up as tightly as possible. The mould was then
slowly heated over a Fletcher gas burner, until a piece of lead lying upon it began to
melt. The brass plug was then inserted in the side hole, and pure skimmed lead
was gently poured in through the neck from an earthen pot until it was full. The
mould was then lifted on to a cold block of iron, but a large blow-pipe was kept
playing on the top of it, the effect of which was that the metal slowly solidified from
below upwards. The progress could be followed by inserting a fine carbon rod, or
more evidently by watching the contraction of the metal in the neck. It was
necessary to add lead from time to time to keep the neck full, and in the case of the
\( 4 \frac{1}{4} \)-inch ball the amount required would have filled about 3 inches of the neck had
it been so long. In this way perfectly sound castings, free from vacuous cavities,
which always form when the metal solidifies on the surface first, are easily obtained;
but to make the metal free from pores, and to close up any such cavities should they
by any possibility exist, the moulds were placed in the hydraulic press immediately
the metal in the neck had become solid, and after removing the brass plug, the steel
plunger was forced down upon its shoulder. The solid metal was thus under great pressure made to flow, and a quantity of wire was forced out of the small side hole. Under these circumstances cavities are impossible, and since pure metal was employed, variations of density were out of the question. It may be worth mentioning here that of all metals in commerce, lead may be obtained of a greater degree of purity than any other. As soon as the pressing had been completed, the mould was removed, and allowed to cool. On being opened the lead ball was found perfect in form, and, so far as it is possible to judge, perfect in every respect, or at any rate so perfect that any departure from such a state cannot produce a disturbance in its gravitative power which is comparable with the limits of accuracy with which the attractions can be observed. I have made four balls of the 4\(\frac{1}{2}\) -inch size, numbered 1, 2, 3, and 4, but I have at present used only numbers 1 and 2. Besides these I have made four of the smaller size of 2\(\frac{1}{4}\) inches in a mould of the same construction and numbered them numbers 6, 7, 8, and 9. To avoid risk of injury, the balls are kept in pairs in four well-made mahogany boxes, with two velvet-lined hemispherical hollows, in each half of each of the boxes. I have made lifters also to raise them by their brass lugs.

I weighed these balls on August 18, 1891, on the large Oertling balance in the South Kensington Museum. Through the kindness of Mr. Chaney I was able to find the true value of all the weights employed, by comparison with the standards at the Standards Office. The weights of the two lead balls made use of, with their included brass ball-holders are, taking due account of the corrections:

\[
\begin{align*}
\text{No. 1} & \quad \ldots \quad 7407.47 \text{ grams.} \\
" & \quad \ldots \quad 7408.15 \quad "
\end{align*}
\]

The lead balls are suspended from the geometrical clamps at the tops of the lid pillars by phosphor-bronze wires, which I drew myself down to the smallest size that I considered safe. This was found by measure to be 0232 inch in diameter. As it had to carry 16.33 lbs., the stress would be one of between 15 and 16 tons to the square inch only, or about one-third of what I had found the wire able to carry. I could not silver-solder the wire into the upper and lower connecting pieces, as the strength was destroyed by annealing, and I found that soft solder allowed it slowly to creep out even when it was soldered into a hole which it nicely fitted, and \(\frac{1}{4}\) inch long. I overcame this minor difficulty by dipping the ends of the wires into copper solution and thickening them by electro-depositing copper until they were just too large to enter the enlarged holes prepared for them. I then drew them through holes in a draw plate down to the right size. They were then sweated into their places, and the end of the wire at the upper end bent over at the bottom of the slot where it just protruded, hammered down and again sweated; while at the lower end a small transverse hole was drilled on each side so as just to touch the side of the wire, and pins driven in, and the whole sweated together. This was done on September 2nd,
1892, and though the wires have carried the balls ever since, they have not broken, stretched, or drawn out. The wire, as it left the draw plate, was free from kinks, and was not allowed to be bent afterwards. As it is stretched so severely, I have assumed that the centre of gravity of the suspended ball is vertically below the axis of the wire, measured at a point nearly 2 inches below its point of support. The actual horizontal distance between the axes of the wires at this level can be determined with the optical compass, with an accuracy of \( \frac{1}{10,000} \) inch; and therefore I maintain that this, the most important of the geometrical determinations, is known with abundant accuracy.

The Small Balls or Cylinders.

Owing to the small size of the attracted masses, I was able to make them of pure gold, a metal which possesses all the advantages of lead, besides increased density and freedom from oxidation or corrosion. As the inside of the central tube of copper in which the gold balls move is polished and electro-gilt, and as they move about an axis which coincides with the axis of this tube, any attractions or disturbances due to difference of electrical potential after contact must be of the smallest order possible. The method of making the gold balls is somewhat similar to that followed in the case of the lead balls, the difference in procedure depending upon the nature of the metal and the reduced size. Mr. Colebrook made for me pairs of hardened steel bars, with ends ground out and polished to true spherical surfaces, each of them just under a hemisphere in extent of surface. These were made in pairs for spheres of diameter, 1.2, 1.25, and 1.3 inch. The quantity of gold necessary for making a ball, plus a small excess for waste, was placed in a hollow in a piece of Bath brick or of prepared charcoal, and heated with an oxy-hydrogen jet with just enough oxygen to melt the gold until it had run down to a clean button. When this was allowed to cool by itself, the surface was drawn in by the contracting centre, and a cavity and dimple were formed. When, however, the flame was gradually withdrawn, or reduced in size, so that the metal solidified from below upwards, a solid button with a perfectly smooth surface was easily obtainable. The button so formed was placed in one of the hemispherical moulds, held in a vice, and covered with the other, which was then given a smart blow with a hammer. The gold was thus compressed to an almost spherical form with an equatorial rib. On being turned over through a right angle, the rib was compressed into the gold, leaving a projecting head on each side, and these were finally compressed into the gold after a further twist through a right angle. The gold was then annealed, and beaten in the moulds with gradually reduced blows, being turned between each blow. When the ball was made practically perfect, it was weighed, and brought down by a very fine file to within 1 milligram of the ultimate weight. It was then annealed and gently beaten again with rapid light blows, being turned between each, until a highly polished perfect sphere was the result. Rubbing with wash-leather and a little rouge brought it to the required weight, when it was
finally gently beaten in the mould. These balls were made in pairs, identical in weight, so far as I could determine with the balance. The smallest weighed 1.2983 grams each. The point of a fine needle, held in a special tool in which the ball was placed, was forced a short way into the gold, and removed, after which the ball was replaced in the dies and compressed again, which process forced down the very small elevation round the little hole, and left a much smaller hole than could be made direct. In order to fasten these balls to their respective fibres, a pin was dipped in shellac varnish and rapidly passed across the end of the fibre. After one or two trials, a semi-microscopic bead of varnish, formed by capillarity, was left just above the end of the fibre. This was then placed in the little hole in the ball, and the latter was placed in a conical hole in a brass blank, which had been warmed in the flame of a spirit lamp. Under the influence of the warmth the little bead slid down, and instantly flashed into vapour as it touched the gold ball. If necessary, a small quantity more varnish could be applied upon the point of a very fine needle. The ball thus attached formed the lower part of a perfect Borda pendulum, there being nothing visible outside the spherical surface. So perfect is this mode of support that when a gold ball is hung up by its fibre, and set in torsional vibration, the image of the window seen reflected on the spherical surface was not seen to move or quiver when examined by a strong lens. The upper end of the fibre was fastened with shellac to the tail of the hook and eye, seen in fig. 7, the length of course being adjusted so that the gold and lead ball would hang at the same level.

There is no question that this is the most perfect method of holding the gold balls, but when I came to the larger size of 0.25 inch, weighing 2.6501 grams, the risk of fracture due to an accidental roll of the ball was increased, and in one case, after a week spent in making all the preliminary measurements, one of the balls drew off, owing to imperfectly dried varnish, and it and its companion and the mirror were all precipitated down the central tube and the torsion fibre was lost. To reduce the risk, I therefore arranged another process which is practically as good and is much safer. A piece of No. 40 copper wire, 3 inch long, weighing 0.0084 gram, was inserted into the hole, and soldered in its place with a scarcely visible amount of solder, the wire and solder weighing exactly 0.001 gram. A calculation of the total attraction of ball and wire, on the supposition that the wire as well as the ball acts upon the centre of the lead ball as if it were concentrated at the centre of the gold ball, shows the error to be only \( \frac{1}{2} \times \frac{1}{10000} \) of the whole, it is therefore of no consequence.

To the side of this wire the quartz fibre was easily fastened with shellac varnish, the amount of shellac used being 0.0001 gram, or even less. I have not made any balls of the largest size, but in the one experiment in which larger masses were employed, have made instead cylinders of gold, 3 inch in diameter and 2587 inch long. These were prepared in a similar manner. Mr. Colebrook made for me a hardened steel cylindrical mould, the inside being lapped out to size and polished. The end was made plane and truly perpendicular to the cylindrical hollow. A polished steel plane
was kept pressed against this face by screw pressure, and a steel plunger, accurately fitting the mould, with a polished plane perpendicular end completed the tool. The required quantity of gold, plus a small quantity for excess, was melted into a button as before, and placed into the mould. The plunger was beaten with a heavy hammer, under the blows of which the solid gold flowed as freely as the lead in the other case, penetrating the fissure between the cylinder and the bottom slab. A second plunger, made of brass, with an exactly central, fine needle point, was then pressed with light blows upon the gold to make a central hole, into which to solder a supporting wire, as in the case of the gold balls. Mr. Edser, of the Royal College of Science, was kind enough to calculate for me, by means of spherical harmonics, the very small difference between the attraction of the cylinder upon a point at the centre of the lead ball, and that which would be exerted if the whole of the mass of the cylinder were concentrated at its centre. The correction is for a greater variation of distance and of inclination from the equatorial plane than can have been met with —00030 of the whole, and this correction is accordingly applied in the one experiment (9) in which the cylinders were employed.

I have not at present referred to the attractions between the suspending wires and the gold balls, and between the suspending quartz fibres and the lead balls. The attractions of the fibres and wires for one another are, of course, infinitesimal to the second degree. Calculation shows that in experiments 4 to 8 and 10 to 12, the attraction of the lead balls for the fibres is to their attraction for the gold balls as 1 is to 204,500, and in the same direction, while the attraction of the gold balls for the wires is to their attraction for the lead balls as 1 is to 115,000, and in the opposite direction. The reversal of the direction is surprising, but it is due to the fact that the most effective part of the fibres is absent in the case of the wires, owing to the large diameter of the lead balls, and, therefore, the action of the long wire on the upper gold ball, which is on the other side, is the preponderating influence. The difference of these two corrections is $\frac{333}{1000}$ of the main effect, and in the opposite direction. I should add, that though the absolute masses of the small balls are known with an accuracy of 1 in 10,000, this is in no way necessary. So long as they are practically alike, it does not matter whether their mass is known or not, as it is ultimately eliminated. I have, however, introduced into the numerical work the actual masses in order to obtain the constants of the fibres and of the mirror, and the viscosity of the air absolutely.

The Beam Mirror and its Attachments.

One of the most important parts of the whole apparatus, and certainly the most difficult to arrive at in perfection, is the combination of beam and mirror which shall support the gold balls definitely in position, and shall, in its capacity as mirror, make it possible to determine their position with the greatest possible accuracy. In my
paper on the radio-micrometer, * I dwelt on the importance of the proper proportioning of the mirror to the rest of the suspended body. Then I only considered its moment of inertia and weight. In the present case these remain important, and there is besides the resistance to motion due to the viscosity of the air, which unfortunately is of the most serious moment. If the usual round mirror is employed, the definition, as is well known, is directly proportional to its diameter—that is, if its figure is perfect. The advantage of a large mirror is somewhat counterbalanced by its weight, which tends to break the fibre, so that lighter balls or a coarser fibre are necessary; by its moment of inertia, which increases the already prolonged period; and by the resistance which it meets with in moving through a viscous atmosphere. As it is important to keep the mirror or mirror and balls swinging as long as possible, in order to determine their periods accurately, a high decrement is most objectionable. By making the mirror in the form of a long bar, I have succeeded in partly reconciling the incompatible conditions, for not only may the weight and moment of inertia be reduced to less than half of that which would be due to a disc of the same diameter, but the definition is decidedly better, as I have proved by experiment, and as is shown by optical theory. I should have said that the definition in a direction parallel to the length of the bar is better, that at right angles being obviously not so good. For the purpose of reading the divisions of a horizontal scale, vertical definition is of consequence only in so far as it is sufficient for the purpose of reading the figures attached. These I had made large with this object. I have already stated that the scale is formed by black lines on a luminous ground. By this means I am able to obtain a degree of reading power which might seem beyond that which a mirror of the size used ought to give. The mirror will form a spurious image of a luminous point of an oblong form, the long dimensions being vertical, and bearing the same relation to the short as the length of the mirror, which is horizontal, bears to its breadth, which is vertical. If the mirror could be made indefinitely long, the image would shrink to a vertical line, and horizontal definition would be perfect. Owing to the limited length of the mirror ('9 inch, about) the width of the spurious image subtends an angle of about 5", and this is the limiting separating power in the horizontal direction. Now, if the scale were made by very fine white or luminous lines upon a dark ground, each line would be seen as a band with shaded edges 5" wide; but, as the angular distance which I have been able to employ from one division to the next is only 14", the lines would have appeared half as broad as the spaces. If the lines on the real scale were of sensible thickness, then the proportion of apparent line to space would have been higher. If, on the other hand, the ground is luminous, the lines are dark and are made rather coarse; the effect of the spreading of the light is to pare off the dark edges, and leave the appearance of a finer line, which, though it is not sharp, is symmetrical, and, as a recurring phenomenon, allows of definite observation to one-tenth of a division, i.e., in the actual case to 1.4". This corresponds to a movement

* 'Phil. Trans.,' Jan., 1889.
of the mirror of \( \cdot 7'' \), and of the balls of \( \frac{350}{1000} \) inch. To this degree of accuracy there is no difficulty in observing; in fact, I might have made the divisions smaller, and still have been able to read to tenths. Of course this perfection is only possible with a very perfect mirror, and for this I applied to Mr. Hilger, who took special pains in preparing several as thin as he dare. Of these, one only, when tested while still round with the large astronomical telescope upon an artificial star, was perfect in its definition, and formed the spurious disc and diffraction rings equally in all directions. This mirror was the one employed in all the experiments up to date. A second one was nearly as good. One made of quartz showed the diffraction rings strongly in three directions only, \( 120^\circ \) apart. In making the test I was careful to notice in which direction the two images, one due to the front surface and the other to the silvered back surface, were separated, owing to the inevitable want of perfect parallelism between the faces. I then cut them in such a direction that the displacement should be vertical, so as to avoid the confusion caused by the superposition of the dim reflection of the scale upon the image under observation. The two good mirrors I slit with a fine steel disc and diamond dust, so as to leave a central bar \( \frac{1}{4} \) inch wide. This gives abundant light, and defines well enough to enable the figures to be read. I found by the use of screens that a bar \( \frac{1}{4} \) inch wide, though it gave enough light, so destroyed the vertical definition that the figures could not be read, and the long and short lines were not so clearly distinguished. I then, with a very sharp-edged brass disc and washed emery, ground in the thickness of each mirror at each end a vertical \( V \), seen in the plan (fig. 7). The bottom was so fine and sharp that a quartz fibre \( \frac{1}{1000} \) inch in diameter would rest definitely in its place. The mirror was cemented with three spots of shellac varnish to the gilt copper support \( O \). This was so formed that the balls could hang by their eye-hooks from the notches at the end of the arms, with the fibres resting in the vertical \( V \) grooves of the mirror. The beam mirror was carried by a quartz fibre, fastened to the point of \( O \) by shellac in all experiments up to No. 3, and soldered to an intermediate tag in the later ones. The details of the soldering process are given in the ‘Phil. Mag.’ for May, 1894. From the lower central hook of the beam mirror the silver counterweight \( K \) may be suspended when the gold balls are removed. This was turned by Mr. Colebrook out of pure silver, which I had prepared by casting and hammering. It is truly cylindrical, and, with the triangular wire hook to which it is soldered, weighs exactly the same as the corresponding pair of balls with their fibres and hooks. Its diameter was measured in several places with a screw micrometer. The weight of the cylinder, of the little hook, and of the solder used were separately determined, and the very small radius of gyration of the hook estimated from its dimensions and form. The period of the mirror was observed \((a)\) with the balls on, \((b)\) with the counterweight on, and \((c)\) alone. From \((a)\) and \((b)\) the unknown moment of inertia of the beam could be determined, and from \(a, b,\) and \(c\) the effect of the stretching upon the rigidity of the fibre could be ascertained. The suppositions made are rather numerous, and are best discussed here.
In the first place it is supposed that the mirror does not change its axis when swung alone or with the balls or counterweight suspended, for, if it does, its unknown moment of inertia will not be a constant, as assumed. Secondly it is supposed that when the gold balls are suspended from the beam mirror, they are rigidly connected with it, or that the mobility of suspension or torsion is so minute as to be equivalent to a rigid suspension. Thirdly, that the counterweight, when suspended from the beam mirror, is rigidly connected with it, and that it rotates about its geometrical axis. It is obvious that however carefully the parts have been made, the suppositions cannot be rigidly true. It is necessary, therefore, to find what order of error is introduced by any possible or observed want of perfection.

It is evident that the axis of rotation of the mirror must always pass through the point at which the quartz fibre leaves it, and that, when it is unloaded, its axis passes through its centre of gravity. As the construction is intended to be symmetrical with respect to this axis, and is so, as far as observation enables one to judge, and as such an axis is an axis of maximum or minimum moment of inertia, the uncertainty in the moment of inertia, due to a small angular displacement, is proportional to the square of the angle, and is altogether beyond the region of experimental certainty. When, however, the balls or counterweight are placed in position, if the construction is not truly symmetrical, the beam mirror will now rotate about an axis which does not pass through its centre of gravity. In an experiment made for the purpose, this displacement, when the larger balls were suspended, was found to be 0.0063 inch, an amount considerably larger than I had expected. In this case the moment of inertia, added to the whole combination on this account, is, weight of beam \( \times 0.0063^2 = 8.44 \times 0.0063^2 = 0.0000335 \text{ inch}^2 \text{ gram} \). The corresponding increase, when the counterweight was added, was \( 8.44 \times 0.012^2 = 0.000012 \text{ inch}^2 \text{ gram} \). Applying these small differences to the observations of Experiment 12, if I may so far anticipate, the torsional rigidity of the suspending fibre is changed from 0.012577 to 0.01257736, so that if this had been overlooked, the error introduced would have been 1 in 33,000. It was not, as a matter of fact, observed until after the conclusion of Experiment 12, and then I placed one of the microscopes so as to see the edge of the lower hook of the beam, and measured the unexpectedly large deviations in the plane of the mirror; those perpendicular to the plane I had always known to be practically inappreciable by the very small change in the position of the observing telescope needed to again see the scale reflected centrally. This insensible correction which tends to make \( G \) seem greater, can only be applied to Experiments 10, 11, and 12, as the fibre met with an accident after Experiment 9, and was re-fastened to the beam. As it cannot be applied to the others, and is far smaller than the uncertainty of the experiment, it is not taken account of in the table.

The rigid attachment of the gold balls to the mirror might seem to be purely imaginary, seeing that they hang from fibres 5 and 11 inches long, and so can lag behind when the mirror is subject to angular acceleration, that they must fly out
owing to their centrifugal force when this acceleration has given rise to an angular velocity, and must be pulled by the gravitation of the lead balls so as to be further apart than supposed. Moreover, since each ball can rotate separately on its own fibre with a period of its own of as much as 6.720 and 9.055 seconds in Experiments 4 to 8 and 10 to 12, they must, in their rotation about their own axes, lag behind the rotation of the mirror when it is being accelerated. The magnitude of these several errors is infinitesimal, or greatly below the limiting accuracy aimed at, and, in all cases, may be calculated and allowed for if necessary. Thus, in Experiment 8, the lower ball in the extreme case of an amplitude of 10,000 divisions, or 100,000 units (I make $\frac{1}{10}$ division the unit, to avoid decimals), is at the middle of the swing thrown out by centrifugal force $\frac{25}{3000000}$ inch, and the upper one about half as much. The linear acceleration on the balls, due to the action of the torsion fibre, is the same as that due to a pendulum nearly six miles long; or, more exactly, 364,335 inches, so that the actual acceleration produced by the fibre in the case of the lower ball is about 1 in 33,000 more than is supposed, and, on the upper ball, about 1 in 70,000. The amount by which the lower ball is pulled outwards by the gravitation of the lead ball next to it, even when that is in its neutral position, where its actual attraction is a maximum, is less than a ten-millionth of an inch. The rotational mobility of the gold balls, however, in Experiments 4 to 8 and 10 to 12, was more than I had intended, and, as I felt that it was important to know precisely what effect this would have upon the result, I referred the problem to Professor Greenhill, who very kindly explained to me exactly how to evaluate it, and, with Professor Minchin, went through the great labour of obtaining and solving the resulting cubic equation. The rigidity of the fibre, in this the worst case, should be diminished by less than 1 in 7850. An increase in the thickness of the two suspending fibres of a few ten-thousandths of an inch, such as I made use of in Experiment 9, would reduce this to the order of 1 in 100,000, or even less, and the complex calculation of this correction would no longer be necessary.

Finally, it is assumed that the counterweight, when it has replaced the gold ball, is also rigidly connected with the mirror and acts axially. With respect to the rigidity of the attachment, it is unnecessary to do more than state that the friction on the suspending hook must be many thousand times greater than the greatest couple ever developed by the torsion fibre, and that, with regard to its axiality, the same remarks that were made with respect to the beam mirror apply with even greater force. There is only one point about which, in consequence of the microscopic examination after Experiment 12, I am not altogether satisfied. It seemed as if the hook suspension was not quite pendularly free so that the counterweight could rest hanging from the beam mirror at a very small angle to its natural position of verticality. This was not observable on the counterweight itself, but only by microscopic examination of the beam. Though the beam hook rarely varied in position by so much as .001 inch, I was able, by using great care in trying to make it rest in
extreme positions, to introduce an uncertainty of position nearly four times as great. I cannot think that any serious discrepancy can have resulted from this, as the uncertainty of moment of inertia would be only a very small fraction of that found in the case of the beam mirror when the balls were suspended. This fault, such as it is, however, I intend to remove in my next experiments, from which I hope, also, to almost entirely exclude the small eccentricities already referred to. For this purpose I may either file the hook rather wider, or, as I think preferable, hang the counterweight by a loop of silk, which will in no way constrain its hanging, but which will be rigid with respect to torsion. I wish, also, to make use of a slightly-silvered torsion fibre, so as to reduce the effect of electrical disturbances if they should be set up by the movements of the air. The square of the corrected period, with the counterweight on, differed more in Experiments 5 and 8 than it should have done, being 1702.35 in Experiment 5, and 1698.73 in Experiment 8. In order to see to what extent this discrepancy may have affected the result, I have calculated the rigidity of the torsion fibre in these two cases with the observations of this quantity reversed, that is, 1698.73 instead of 1702.35, and vice versa. The effect upon the result is 1 part in 10,600, so that if all the error is in one observation only, the other one is on this account alone less than \( \frac{1}{10000} \) in error. As any sticking of the counterweight would tend to increase the moment of inertia, and hence the period, I am inclined to look with greater favour on the smaller observation, but the difference, in any case, is considerably less than the actual differences found in the final results.

In connection with the beam mirror, it is convenient here to describe the means provided for keeping it under control from the telescope without entering the shielded corner of the vault.

Below the apparatus, figs. 1 and 2, may be seen a tube terminating in a bent glass pipe which enters the hollow screw s. This is joined to a narrow piece of composition piping, which is carried across the interval between the two tables by the wooden bar which serves to protect the light driving cord, and, at the eyepiece of the telescope T, terminates in a mouthpiece. Where observations of deflection and period are being made, air may be drawn through the tube causing a very gentle indraught through the tube of the window, fig. 12. This acting on one end of the mirror produces upon it a couple which may be employed to bring it to rest or to get up a swing of large amplitude. The extreme precision and delicacy of this process is best explained by considering an electrical analogue. The window tube, fig. 12, acts as a moderate resistance, the open space between the glass tube and the large hole in the screw as a short circuit or very low resistance, and the long tube across the room as a high resistance again. The electromotive force is the suction of the mouth. Owing to the high resistance of the long tube, but a feeble effect is felt at the glass end, and this is practically entirely satisfied by the low resistance leak. The available electromotive force acting upon the resistance of the window tube is therefore very small, and in consequence the current acting on the needle is similarly minute. So delicate
is this that it is quite easy by pinching the tube properly with the fingers to bring the movements of the mirror, when the counterweight but not the balls are suspended, down to one unit, corresponding to \( \frac{1}{75,000} \) inch movement of the gold balls if they were in their place.

Conclusion of Part I.

The apparatus and optical compass were made by the Cambridge Scientific Instrument Company. I cannot lose this opportunity of expressing my great indebtedness to Mr. Pye, who, in the absence of Mr. Darwin through illness, entered into every detail with the greatest care and faithfully carried out all the directions as to modes of construction upon which, after consultation with him, I finally decided.

As already mentioned, Mr. Colebrook constructed the special tools and the very numerous extraneous apparatus. He also made all the special windows. Mr. Munro made the tools for compressing the lead balls, and being his work they are of course accurate in the highest degree. Mr. Stanley undertook the large scale, but though the execution of the etching is excellent, the accuracy is not good. This, however, matters little, for the errors are eliminated by the calibration.

The actual work of making the gold balls, the lead balls, the finish of the beam mirror, the quartz fibre work, the gilding and polishing of the inside of the central tube, and a great deal of the general fittings I did myself, either alone or with the help of Mr. Chapman and Mr. Colebrook of the Physical Laboratory.

The apparatus, which belongs to the Science Collection of the South Kensington Museum, will, I hope, on the completion of the experiments, be set up in a special place in the Museum so that it may be seen in action by anyone interested. I intend to leave also permanently in the Museum a series of photographs of the apparatus as it appears in situ when each one of the operations is being carried out. Besides this, the note books and all the calculations will be left there permanently so that reference may be made to them in case any point is insufficiently explained.

Part II.

The Mode of Procedure.

The actual method of carrying out the experiment, though in the main obvious to any one who has read the first part of this paper, is nevertheless in some particulars by no means evident. As, moreover, a careful explanation of the several operations and the purposes which they serve will make the mere numerical details of the actual experiments, which form the third part of the paper, more intelligible, I shall describe them in order, under distinguishing numbers.

The operations, as described, are fourteen in number, but they are of very different
importance, and the time required for carrying them out differs also very much. Some few need only to be performed on the first putting together of the apparatus.

Operation 1.

After placing the instrument in the selected spot, with its centre tube vertically below the edge of the central overhead pulley, it is to be levelled accurately by placing a spirit level on the lid, and adjusting the levelling screws, until the bubble occupies the same position in the tube when the lid, carrying with it the level, is slowly made to revolve. Fix also the scale and large telescope in position.

Operation 2.

Hang up the lead balls by their wires and upper supporting pieces, pinning the latter to the thickened lower ends of the two steel bands. These are carried over the flat-rimmed pulleys, and carry at their other ends counter-weights, so that the balls will remain suspended at any level. If the central tube is not in position the three readings, \(a\), \(b\), and \(c\), fig. A, are made with the cathetometer, and thus the true distance from \(a\) to the centre of the lead ball, when the wire is stretched by the weight of the latter, is known. If, after one experiment, it is desired to make this measure, but not to move the central tube, since it is impossible to remove the lead balls completely, they must be left suspended at such a height that the \(b\) of each is visible. This can be accomplished without taking away the lid and lid pillars, since they can be left suspended by their counterweight at such a height that the \(a\) of the (ultimately) upper ball is below the lid, while the \(a\) of the (ultimately) lower ball is above its lid pillar. Since all hang freely without touching one another, the \(a\)'s and \(b\)'s can be determined, and on adding the known radius of the lead balls, the distances \(ah\) are known.

Operation 3.

Hang the gold balls by their eye hooks upon a pin driven into any temporary stand. Measure with the cathetometer the three positions \(d\), \(e\), and \(f\) of each, fig. B. From
these the distances \( dg \) can be determined when the fibres are stretched by the weight of the balls. Also find their individual torsion periods by the method of coincidences,

![Fig. B.](image)

watching them with the cathetometer telescope, and listening to the clock. This latter is needed for the purpose of calculating the very small correction (p. 35) which should be evanescent. The cathetometer measures can be made with an accuracy of two or three-hundredths of a millim., and this, as will appear when the figures are examined, is more than abundantly accurate.

**Operation 4.**

Put the lead balls in the apparatus, fix the central tube in place, with its front window facing the scale, let the gold balls down the central tube, and hang them on the side hooks, place the lid in position; having marked one side of the lead balls in some distinguishing manner (a very small spot of shellac varnish is what I used), suspend them with these marks pointing in some definite direction, e.g., inwards; let down the mirror by its torsion fibre, and adjust the torsion head so that it hangs approximately centrally, and at a convenient height.

**Operation 5.**

Find, as already described, the division at which a perpendicular from the axis of the tube falls upon the scale. Twist round the central tube, if necessary, until the window reflects a light placed behind this division into the large telescope.

**Operation 6.**

Find the optical distance in terms of the corrected scale division from the silvered surface of the mirror to the foot of the perpendicular upon the scale, and thus find the angular measure corresponding to any observed deflection.

The details of this process are sufficiently described under the heading *The Steel Tape and its Accessories* (p. 17).

**Operation 7.**

Make cathetometer readings of \( a, a \) and \( d, d \). Subtract from these the corre-
sponding quantities found in operations 2 and 3, \( ah \) and \( dg \), and thus find the levels of the centres of the gold and of the lead balls. If the gold balls are on the whole high or low, lower or raise the torsion rod the necessary amount and re-measure \( a, a \) and \( d, d \).

**Operation 8.**

If the mirror rests so that the foot of the perpendicular is about the position of rest as seen by reflection in the telescope, when the lead balls are, so far as it is possible to judge, in the same plane as the gold balls, all is ready for the next operation; otherwise it will be necessary to turn the support of the torsion rod, which will not raise or lower it, until observation at the telescope shows that this is the case. The mirror will then be symmetrically placed with respect to the window.

**Operation 9.**

This is a long operation carried out with the optical compass, the object being to find the horizontal distances between the axes of the wires and between the axes of the fibres, to centre the torsion fibre with respect to the axis of the instrument, and to find the corresponding readings of the vernier of the lid and of the glass scale seen by reflection in the telescope when the plane of the wires and fibres is identical. Owing to the great length of this operation, the description of it is divided into sections.

**Section a.**—Remove the two pillars RR from the lid, and the first spur-wheel of the driving train \( W \), which is made to simply lift off. Put the optical compass in its place on the lid so that the line of traverse is apparently parallel to the line joining the wires.

Focus the positive eye-piece of each microscope upon its cross-wire or scale, and then shift the focussing collars \( c \) of each, so that when the microscopes change places in the same groove and are pressed up to their collars, they are each in focus on the same object.

**Section b.**—Using one microscope in any one groove of one of the traversing slides \( T_1 \) or \( T_2 \), focus alternately on the edges of the two wires, using the focussing screw \( S_3 \) to move both the same way, and turning the base of the optical compass upon the lid to move them opposite ways. When both are found in exact focus the line of traverse is parallel to the plane joining the axes of the wires.

**Section c.**—Measure this distance. To do this the two traversing slides are placed together, and the fine steel spring passed through the hole in their \( V \)'s. The spring is then stretched and prevented from contracting by a pin passed through it at one end. The two slides \( T_1, T_2 \) then are pulled together by the spring, but are separated more or less by the adjusting screw cone \( S_4 \). The two microscopes are laid in the outer grooves (or the middle pair in case a 4-inch distance has to be measured), and the slides moved until each is directed upon one side of the corresponding wire. The
final exact adjustments are easy of execution, for the focussing screw $S_3$ supplies a slow fore and aft motion, while the corresponding slow lateral movement is given by the screw cone $S_1$. In order to allow one only of the traversing slides to move, the fingers of one hand are made to rest upon the slide which is to be kept still, and thus its friction on the base increased, the other one then only moves. When both microscopes are focussed upon (say) the right or apparent left sides of the wires, and their cross-wires are directed upon them also, the focussing slide is withdrawn about an inch, and the focussing block $b$ put into its place. The slide is then pushed forward until the focussing screw rests against the focussing block. The small glass scale is then placed so as to rest against the two parallelizing screws $S_2, S_2$, and against the micrometer screw $S_1$, and $S_2, S_2$ are moved until the scale is in focus in both microscopes at the same time. $S_1$ is then turned until the intended zero of the scale '04 is on the cross-wire of the left microscope and its head is read: it is then turned forward a fraction of a turn until a division at the other end of the scale 6'03 or 6'04 is on the cross-wire at that end. The amount of movement indicated by the head of the screw $S_1$, added to the tabulated distance from '04 to 6'03 or 6'04, is the distance from the right side of one wire to the right side of the other. If the eye-piece micrometer is used instead of the cross-wire, then '04 is brought in the central division of the left-hand microscope, and the micrometer readings of the divisions 6'03 and 6'04, or 6'04 and 6'03, are taken in the right microscope. Knowing the tabulated length of either of these divisions and the number of eye-piece divisions corresponding to it, the amount to be added to the tabulated distance between '04 and the lower of the two observed, is readily found. The distance between the left sides of the wires is found in the same way, and the mean of the two is taken for the distance between their axes. The thicknesses of the wires are also found by subtracting the readings of the apparent right from the readings of the apparent left sides, remembering that there are two whole turns of the screw. After each operation the focussing block is moved round, and the focussing slide moved up so as to bring the wires into view. If they are not exactly on the cross-wire as before, the measure is rejected and a new one taken, but this is rarely the case.

The example taken from Experiment 3 does not show the confirmatory observations made with the eye-piece micrometer, for at that time the micrometer scales had not been made. As I still rely upon the screw measure of the fractions and only take the eye-piece micrometer readings to satisfy myself that the screw observations have been correctly worked, this example will serve as well as a later one.
The measures of wires with optical compass.

<table>
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<tr>
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<tbody>
<tr>
<td>Apparent right</td>
<td>Right . . .</td>
<td>6.03</td>
<td>641</td>
<td>0.029</td>
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<tr>
<td>&quot;</td>
<td>Left . .</td>
<td>0.04 (+4)</td>
<td>357</td>
<td>+0.00025</td>
</tr>
<tr>
<td>&quot;</td>
<td>Right (605+2)</td>
<td>6.03</td>
<td>955</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>Left . .</td>
<td>0.04 (+4)</td>
<td>357</td>
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<table>
<thead>
<tr>
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<th>Thickness.</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
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<tr>
<td>0.03377</td>
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<td>0.00029</td>
</tr>
<tr>
<td>5.98598</td>
<td>5.98612</td>
<td>0.02328</td>
</tr>
<tr>
<td>5.98612</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Mean . 5.98605 centre to centre. + 0.00025 correction. | 5.986075 corrected value. |

The (+ 4) after '04 indicates that when the right microscope was exactly on the division 6.03, the left one was, by eye estimation, at '044, or \( \frac{1}{6} \) of a division above '04. Since also the screw-head reading has passed 1000, or a complete turn, and has risen in the two cases to 029 and 357, '05 is the quantity that must be written in the subtraction below to find the distances from side to side of the wires.

\((6.05 + 2)\) means that 6.05 was the division seen when the scale was put in its former place and that two whole turns of the screw were needed to bring 6.03 into view again. It was because there was only one division at the supposed zero '04, that the scale had to be pushed forward so as to bring 6.03 into view again, and '04 and 6.03 were used to measure the apparent left (but really right) sides of the wires.

**Section d.**—Place the two microscopes in the centre pair of grooves and bring them both in succession to focus on the same wire, adjust the focussing collars, if necessary, so that when pushed up to their collars they are each in exact focus. Having the proper back window, figs. 13, 14, in position, withdraw the microscope and move the traversing slides till the microscope will be able to slide forward and view the fibres. Push both up to their collars and move laterally until the fibres are found. If, as is probable, they are out of focus, ascertain by moving either microscope by hand in its grooves whether the error of focus is in the same direction for both. If it is not, slowly turn the lid, using a lever bearing upon the pin of the first wheel of the train and entering the nearest tooth on the edge of the lid. This
NEWTONIAN CONSTANT OF GRAVITATION.

does not affect the parallelism of the line of traverse with the plane of the wires, for the optical compass is carried round with the lid. When the fibres seem about equally out of focus and in the same direction, bring them towards or away from the microscopes, as may be necessary, by the adjusting screws of the torsion head. However carefully this may be done, the suspended beam and gold balls are sure to be set swinging slightly as a pendulum. This is easily overcome by resting a wax taper or very flexible piece of wood against the central tube, and while watching the motion in the microscope bearing very lightly upon it in time with the oscillations. There is no difficulty in reducing the motion to the $\frac{1}{10000}$ inch in a very short time. If a torsional swing has begun, there is nothing to be done except to wait until the amplitude is reduced to a very small amount. It is impossible to obtain real quiet in this sense, as owing to gravitation the observer’s body and the gold balls will attract one another unequally. After one or two trials the two fibres will be found simultaneously in focus, at any rate, if not continuously owing to the small torsional oscillations, yet between the elongations at successive half periods. I prefer to leave the apparatus at this stage and to return after an hour, when the mirror is more quiet, to verify the accuracy of focus. If this is correct since the focussing screw has not been touched, the plane of the fibres coincides with the plane of the wires. If more than a very small focussing correction is made, Operation 8 will have to be repeated afterwards.

Section e.—Read the great scale in the telescope and take the vernier reading of the lid. Then, since the wires and fibres are in the same plane, the lid reading and corresponding scale reading are known for one position, and, since the angular value of a scale division is known, also for all positions.

Section f.—Measure the distance between the fibres and their thicknesses, using exactly the same procedure as described under Section e. I may mention here that as the beam mirror is only ‘9 instead of 1 inch as intended, the traversing slides as made would not come near enough together for both fibres to be seen at the same time. I therefore made use of the traversing slides in their other position, i.e., with $T_1$ to the right of $T_2$ instead of to the left, after having had the right side of $T_2$ reduced by slot drilling so as to allow the now inner grooves to come $\frac{1}{3}$ inch nearer to one another. The change from one position to the other is made in a moment.
Example.—Measures of Fibres with Optical Compass.

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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Apparent right</td>
<td>Right</td>
<td>3.45</td>
<td>439</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>Left</td>
<td>2.55 (+ 7)</td>
<td>078</td>
<td>-0.0033</td>
</tr>
<tr>
<td>&quot; left</td>
<td>Right</td>
<td>3.45</td>
<td>545</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>Left</td>
<td>2.55 (+ 7)</td>
<td>180</td>
<td></td>
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</table>

<table>
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<th>Apparent right edge.</th>
<th>Thickness.</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>Left.</td>
</tr>
<tr>
<td>3.45545</td>
<td>3.45439</td>
<td>180</td>
</tr>
<tr>
<td>2.50180</td>
<td>2.50078</td>
<td>078</td>
</tr>
<tr>
<td>-0.89365</td>
<td>-0.89361</td>
<td>0.00102</td>
</tr>
<tr>
<td>-0.89361</td>
<td>-0.89363</td>
<td></td>
</tr>
</tbody>
</table>

Mean . . . -0.89330 centre to centre.
-0.00033 correction.

-0.89330 corrected value.

Section g.—Set one microscope to see one fibre and the other in the proper groove in the traversing slide to see one wire. Measure, as in Section c, the distance from one edge of one fibre to one edge of one wire. Then move the traversing slide so as to measure the corresponding interval on the other side. Knowing the two intervals, the thicknesses of the wires and of the fibres, and the distance between the axes of the wires (2 R), and between the axes of the fibres (2 r), it is at once known to what extent the pair of fibres are eccentric with respect to the pair of wires. Without touching the back adjusting screw of the torsion head, screw the other two until one of the fibres has moved the right amount as measured by the eyepiece micrometer. If a movement of more than a few thousandths of an inch is necessary, it is best to re-measure the right and left intervals, and again adjust. When this is done the two fibres are in the same plane as the wires and exactly half-way between them.

If now the construction were perfect the torsion fibre would be in the axis of the instrument, and the lead balls would move centrally round it, but if either the two radii of movement of the gold balls r, r or the two radii of movement of the lead balls R, R differ from one another, or if the two lead balls hang from points which
are not diametrically opposed to one another, then the lead balls will not rotate about the torsion fibre as an axis. If, however, the optical compass is removed and the lid is turned round 180°, and the measurement repeated, then half the movement necessary to bring the fibres into focus as measured by the head of the focussing screw is the diametrical inaccuracy of the lead balls, and half the inequality of the right and left intervals is their eccentricity with respect to their mechanical axis measured in their own plane. The torsion head may now be moved half of each of these amounts separately, and then the vertical line half way between the pair of fibres, which by construction is necessarily the same as the torsion fibre within less than $\frac{1}{1000}$ inch, is also in the mechanical axis about which the lead balls actually turn.

**Examples.—Plane of Fibres and Wires.**

Focus for wires, ‘05 on focussing screw.

" " fibres, ‘25 " "

Therefore the fibres are behind (away from microscope) the wires by $\frac{2}{50} = 0.04$ inch.

_Eccentricity of Pair of Fibres._—After setting the pair of microscopes to one interval and sliding to the other, the left appears in the eye-piece to be smaller than the right by about ‘007 inch.

By measurement it is found to be ‘00792 less, or the pair of quartz fibres are ‘00396 out of centre.

The necessary observations are :

| 5.98607 | Centre to centre, wires. |
| 0.9330 | Centre to centre, fibres. |
| 0.02314 | Thickness right wire. |
| 6.90251 | |
| 0.0102 | Thickness left fibre. |
| 2)6.90149 | |
| 3.45074 | Mean of right and left intervals. |
| 3.45470 | Right edge left fibre to right side right wire. |
| ‘00396 | Excess of right interval above mean. |
| ‘00792 | Right interval greater than left. |

**Operation 10.**

Prepare for observations of deflection and period. Remove the optical compass and replace the windows by fig. 12 at the back and fig. 11 in front. Place the tubular screens, fig. 15, in position. Screw in the pillars R, R, and arrange the guys, &c.
and counterweight so as to reduce the weight of the lids and balls and therefore their friction to a small amount. Place the first of the train of wheels W in place. See that the string operating the driving gear is in place, and that the india-rubber tube under the apparatus is connected to the composition tube going to the telescope. Place the two halves of the octagon house in position, and fill up the open gap where it overhangs the table at the back with a duster. See that the little electric lamp inside the house is properly placed to illuminate the vernier. Remove all superfluous apparatus from the table. Place the felt screen in position, and, when all is proved to be in working order, leave, if possible, for three days to acquire a uniform temperature.

The angle through which the lead balls must be turned in order to produce the maximum deflection I had found in a preliminary calculation, completed before the apparatus was made, in which 2 R was made 6 inches, 2 r 1 inch, and the difference of levels 6 inches, to be 61° 15', and the effect of an error of 15' at this position to be 1 part in 280,000. With the actual apparatus, in which 2 r is less than 1 inch, I found by experiment the angle of greatest effect to be 65°, which is that adopted. Knowing the vernier reading corresponding to the observed scale reading when there is no deflection observable with the optical compass, i.e., when the lead and gold balls are in the same plane, or in the neutral position, and taking this provisionally as a position of no deflection, move the lid in one direction through an angle of 65° by turning the handle of the wheel d by the telescope round 115 times. The exact setting of the lid is finally accomplished by lighting the electric lamp in the octagon house, and observing the vernier with the small telescope t. Three or more elongations of the apparently moving scale are now read in the large telescope, and then the wheel d is turned 125 times back, and, when the mirror is approaching its position of rest, the remaining 105 turns are given to the handle, which leaves the balls 65° on the other side of the neutral point, and the mirror oscillating through 50 divisions of the scale, or even less. The vernier reading must be correctly set by the use of the electric lamp, little telescope, and handle d, as before. Three or more elongations are again taken. The elongations are corrected, and from the corrected elongations the positions of rest, when the lead balls are in their + and in their − positions, are calculated. If the supposed neutral position had been accurately found, its scale reading would be exactly half way between the + and − position of rest. If, as is probable, it is not quite accurate, then, since the variation of the position of rest of the mirror is hardly observable when the lid is moved even so much as 1° from its position of maximum effect, while such an uncertainty of position is not possible in the provisional setting, all that has to be done is to bring the lid into such a position that the mirror is at rest exactly half way between its extreme + and − positions already observed. It is not sufficient to move the lead balls through an angle corresponding to the error, because, though at the neutral position the smallest variation produces the greatest effect upon the gold balls, they do not follow it abso-
lately. I always take two observations with the telescope of the position of rest of the gold balls when the vernier readings differ by about $2^\circ$ at the neutral position, and thus, knowing how many scale-divisions deflection are produced at this position by a movement of the lead balls of $1^\circ$, I am able at once to find the vernier reading of the true neutral position (N). Then, when the vernier reading is made N + $65^\circ$ or N − $65^\circ$, the deflections in the + and − directions are found to be the same within $\frac{1}{10}$ per cent., from which it is evident that the + and − positions have been set truly, with a superabundant degree of accuracy. This preliminary determination I generally make the night before the deflections and periods are determined, which in Oxford is best done on Sunday night between midnight and 6 A.M. The daytime, of course, is out of the question, owing to the rattling traffic on the stones in St. Giles', about a quarter of a mile away; and all nights except Sunday night the railway people are engaged making up trains and shunting, which is more continuous and disturbing to the steadiness of the ground than a passing train. Even these come through at intervals on a Sunday night, and this limits the accuracy with which the periods can be observed. All having been prepared for the Sunday night during the previous week, the room is shut up all day, and at midnight or a little later the actual observations of deflection and period are begun.

For a long night's work without accidents, I am able to take two or three sets of observations alternately at each of the + and − positions, with one at the neutral position; one period at each of the + and − positions, lasting about 45 minutes, and occasionally one at the neutral position, lasting about 15 minutes, and finally two or three sets alternately at each of the + and − positions, followed rarely by one, or even two, periods of 30 to 45 minutes. For each set of observations at the + and − position, I observe six consecutive elongations, and sometimes eight if I am disturbed by the trains. I do not begin them until the apparatus has quieted down from any very small tremor which the rotation of the lid may have set up.

In observing the period, the point of rest is known from previous observation. A conspicuous pointer tapering to a point, which can be inserted into any division, or if between can be read to a tenth of a division, is placed at the point of rest. Air is gently drawn from the mouthpiece for a quarter period and then stopped. According to the speed at which the pointer flashes past I determine whether or not to draw air again. If I do, I begin about a quarter period after the transit, and continue until the next transit, or a quarter period longer still, according to the velocity of the transit. It is most important not to begin or leave off drawing the air suddenly, lest a quick period movement, of which there are five independent of one another, should be set up in the mirror. I begin very gently, gradually increase and gradually leave off, the result of which is a beautifully steady motion of the mobile system, extending far beyond the limits of the scale. I then start the drum and make a dozen marks with the key in rapid succession, to indicate the beginning of an observation. At each transit, the key is pressed suddenly and then
Fig. C.
NEWTONIAN CONSTANT OF GRAVITATION.

held down for one second, which produces a "transit mark," the purpose of which is to indicate that the previous dash was made at a transit of the pointer. Immediately afterwards I note in the book an arrow showing the direction of motion. Every transit is thus marked during the first stage, which lasts 10 or 15 minutes. In order to know the actual time of any of the minute marks, I hold the key down once at a minute for six seconds and thus produce "time mark." This also is noted in its proper place in the book with the time. To still further make sure of the place in the book which corresponds to any place on the smoked drum, I occasionally make a "castle mark," that is, hold the key down during alternate seconds four or five times, and note that also in the book. The proper sequence of time marks, castle marks, and transit marks, is sufficient to make it evident afterwards to which arrow in the book any particular transit mark belongs. During this stage it is not possible to take the elongations as they are off the scale. I then leave the apparatus to itself for about 20 minutes after first stopping the drum. On my return I start the drum, secure another time mark, and every transit, as before, with a castle mark somewhere for distinction, but now the elongations being observable I note them in the book at the same time. Following the practice of Professor Cornu, but on an extended scale, I take the transits of the chief divisions at first of every 1000 divisions, then of every 100, and after a time of every 10. These are distinguished on the drum by four rapidly repeated dashes after a 1000, three after a 500, two after a 100, one after a 50, and none after a 10. I cannot take single divisions as they pass by so rapidly. I have not used these marks except in rare instances, but they are available for reduction in case time for the very tedious calculation could be found. Fig. C is a full size reproduction of a portion of the sheet of October 1st, 1893, after I had gone over it and scratched in the actual times. The different classes of marks are all to be seen. I do not, as a rule, find it possible to put in arrows while writing elongations, and marking transits of divisions as well as of the pointer. Their existence is understood between elongations. In addition, I generally place a letter or word to distinguish good observations of transits: from bad, thus: — g., — v.g., — bad, or — 04' late. I do not think the v.g. observations can be more than .01 second in error, or the g. more than .02 or .03 second. Those unmarked might be perhaps as much as .1 second, though they may also be good, but those marked bad would probably be more. If it were not for the high period tremor set up by the trains, which prevent good observations when the amplitude is less than about 40 divisions, I should expect to obtain a higher degree of accuracy in the periods than are actually obtainable. I sometimes take observations of deflection and period on more than one night.

Operation 11.

Transfer the gold balls to the side hooks, and leave for a day, if possible, to quiet. Find the deflection, if any, produced upon the mirror alone, by moving the lid and

MDCCCV.—A.
lead balls from the + to the − positions. Find also with large amplitude, the exact period with and without the counterweight, using the drum and following all the details given in operation 10. At this stage it is convenient to set up the cathetometer and measure the stretching of the torsion fibres by observation on the bottom hook of the mirror. This is not necessary for the purpose of finding G, but it is of interest as bearing upon the elastic properties of quartz fibres.

Operation 12.

Turn the lid round to the neutral position. Place the steel bands on the flat-rimmed pulleys. Pin to the ball holders, and hang on at the other end the counterweight. Raise the balls about \(\frac{1}{8}\) inch, turn them individually through 60° and let the geometrical clamps down through the triangular orifices of the lid pillars, until the balls rest on the india-rubber rings on the base. Raise the lid, leaving it balanced in the air by its counterpoise, and after removing the two counterweights and the holding pins, take away the steel bands. Let down the lid again. Partly balance it as before. Put screens and octagon house in position as before, and after a day or two take deflections, if any, when the lid and lid pillars are moved between the + and − positions. Three sets of six elongations at least should be taken at each position.

Operation 13.

Re-suspend the gold balls in the same position as before, and find the deflection of the mirror, if any produced, by moving the lid and lid pillars from the + to the − positions.

Operation 14.

Take the focussing collar off one microscope of the optical compass, and slide it on to the nose end of the other, so as to raise it high enough to see the side of the bottom hook of the beam mirror. Remove the front lens of the object-glass, which reduces the magnifying power to rather less than one-half. Set the optical compass so that the vertical tangent to the curve of the lower hook is on the zero of the micrometer scale in the eye-piece, that is when the mirror alone is freely suspended. Hang on the counter-weight and take the scale reading. Hang on the gold balls instead of the counter-weight and take the scale reading again. The object of this is to find to what extent, if any, the axis of rotation of the beam changes when the balls or the counterweight are suspended (see p. 34).
The calculation of the results from the figures obtained by observation is divided into four sections:—(1.) The deflections and periods; (2.) The geometry of the apparatus; (3.) The dynamics of the moving system; and (4.) The combination of these resulting in the determination of G, the Newtonian constant of gravitation, and indirectly of \( \Delta \), the mean density of the earth. In the preparation of this part I have been greatly helped by Mr. S. G. Starling, of the Royal College of Science, who has carried out the laborious numerical calculations.

1. The Deflections and Periods.

The treatment of the figures obtained during the observations of deflection will be best explained by an example. I give two consecutive sets, one the worst obtained the whole night, and the other a particularly good one, but others obtained that night were practically as good.

Sept. 17, 1893.

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<thead>
<tr>
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<th>13h. 0m.</th>
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<tr>
<td>24007</td>
<td>-24</td>
<td>21883</td>
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<tr>
<td>24193</td>
<td>-26</td>
<td>24167</td>
</tr>
<tr>
<td>24789</td>
<td>-24</td>
<td>24765</td>
</tr>
<tr>
<td>24922</td>
<td>-26</td>
<td>24266</td>
</tr>
<tr>
<td>24709*</td>
<td>-25</td>
<td>24684</td>
</tr>
<tr>
<td>24355†</td>
<td>-25.5</td>
<td>24329.5</td>
</tr>
<tr>
<td>24654†</td>
<td>-26</td>
<td>24628</td>
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</tr>
<tr>
<td>21197</td>
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* A short period oscillation or tremor, set up probably by a passing train.
† A pendular oscillation, set up probably by a passing train.
A represents the lid reading differing from 85°, the neutral position, by the azimuth 65° of the lead balls. The actual time of the beginning of a set is next marked and then the temperature of a thermometer set up close to the apparatus. This is illuminated and read by the same means that are provided for reading the lid vernier.

The first column of figures are observed elongations expressed in tenths of scale-divisions. The second column contains the scale corrections, in which are included both the calibration and the circular errors. The third column are the corrected elongations, the fourth the differences of these or amplitudes, the fifth the ratio of these or the decrements, in the sixth are the quotients of each amplitude by 1 + the following decrement. The last column contains the algebraical sums of the corresponding numbers in the third and sixth columns. They represent the points of rest during the course of the oscillation. Each series gives a mean point of rest of which a dozen or more may be obtained in one night. I prefer to arrange all the individual points of rest as well as the mean points in their proper places in a diagram, of which abscisse represent the hour and the ordinates the points of rest, but on a very large vertical scale. The one of these for the evening's work chosen for illustration is shown in fig. D, from which it will be seen that a gap of 368 inches has been cut out to save room. The series of mean points of rest are shown in the following table:—
The deflections \( P \) are obtained by taking these in groups of consecutive threes, to allow as far as possible for steady creeping of the zero. It will be seen that in the present instances there is nothing very definite that can be attributed to this.

The four deflections obtained in this way before the time interval are—

\[
3696.5 \\
3696.6 \\
3696.0 \\
3696.8
\]

The two after are—

\[
(3697.7) \\
3696.0
\]

As the mean point of rest 20793.7 was taken immediately after the oscillations of large amplitude produced by the air draught and was definitely slightly disturbed, I have not included the resulting deflection 3697.7 in the series from which the true deflection on that particular night was determined. The agreement is exceedingly close, so that the mean of the five values \( P = 3696.4 \) may be taken with considerable confidence.

The observations on this night were rather more consistent than usual, owing, as I believe, to the very unusual quiet noticed at the time.

I only took one observation of period on this night, recorded as follows:
If the pointer had been found to have been definitely out of place, but, of course, by a small amount, I should have corrected the observed times of transit by a series of alternate + and − quantities, calculated from the amplitude, period, and error of position. In the present case, owing to disturbance, the point of rest showed an uncertainty of nearly half a division, and I could not be sure from these observations that the pointer was not placed that much in error. On the other hand, after subtracting the time of each transit from that above, the series of observed half periods show a small, fairly regular, increasing and alternating second difference, which is in itself a sign that the pointer was very slightly on one side of the true position of rest. If no account is taken of this, the half period deduced from the first and last observation is found to be

\[ 96.650 \text{ seconds} \]

from the first observation marked \( g \) to the last marked \( g \) it is

\[ 96.649 \text{ seconds} \]
and if the times of transit are corrected by one quarter of their second difference, so as to approximate to the times of transit of the point of rest, the half period over the whole series becomes

\[ 96.645 \text{ seconds.} \]

The object of examining so many transits is not so much with the idea of applying methods of least squares or of otherwise equalising errors, but mainly to see that the oscillation is going on regularly and that no sudden disturbance has arisen which, if it were undetected at the time, might become lost and yet leave the result in error by an observable amount. I find that in the present instance I did not try to improve upon the observations by arithmetical manipulation, and that 96.650 was taken as the observed half-period. Two small quantities had to be subtracted from this, one a correction of \(-0.0034\) due to a gaining rate of two seconds a day of the clock, and one of \(-1.508\) on account of the damping effect of atmospheric resistance. The true whole period for no damping then becomes 192.992 seconds, and its square 37245.9 is the quantity which is finally made use of in the dynamical calculation. It is recorded as \(T_a^2\), the square of the time with the balls on. In a similar manner \(T_c^2\) is found when the counterweight is on, and \(T_o^2\) when the mirror alone is swinging.

Under this heading the deflections produced in Operations 11, 12, 13 must be considered. The deflection in Operation 10 is due to four possible attractions:

1. Lead balls, &c., on gold balls.
2. Lid and permanent fixtures, &c., on gold balls.
3. Lead balls, &c., on beam mirror.
4. Lid and permanent fixtures, &c., on beam mirror.

The deflection, if any, of Operation 11, is due to (3) and (4) above. Similarly the deflection produced by Operation 12 is due to (4) alone, and of Operation 13 to (2) and (4). Knowing, therefore \((1) + (2) + (3) + (4); (3) + (4); (4); and (2) + (4); (1), (2), (3) and (4) are separately determined.

I have on two occasions since Experiment 3 was completed (which was of a semiprovisional nature) carried out the deflection observations of Operation 11. On September 1, 1893, \(1.5\) units or \(15\) division was obtained. There was a very slight \(+\) creep. On September 11, with no creep and very consistent behaviour, \(5\) unit or \(0.05\) division was obtained. I do not know whether I should take \(5\) or \(1\) unit. The difference is beyond what can be observed with any certainty.

I find that the lid was turned \(180^\circ\) between the two experiments, but this could not make any difference. I have taken \(1\) unit as the deflection in Experiments 4 to 12, and have calculated what it should be in Experiment 3.

Most careful observations on September 2 and 3, 1893, failed to show any deflec-
tion under Operations 12 and 13; certainly not 1, and not, apparently, \( \cdot 1 \) unit. From this it will be evident that since

\[
\begin{align*}
(3) + (4) &= 1, \\
(4) &= 0, \\
(2) + (4) &= 0,
\end{align*}
\]

(2) = 0, (3) = 1, and (4) = 0. Therefore 1 unit must be subtracted from the observed deflection of Operation 10 in all experiments after No. 3. It is for this reason that the numbers under P in Table I., p. 63, differ very slightly from the observed deflections.

2. The Geometry of the Apparatus.

In this part of the calculation I find the exact relative positions of the several gravitating bodies, from which the couple twisting the fibre may be found in terms of G. Thus, the couple = QG. As before, the process followed will be most readily explained by giving an example.
NEWTONIAN CONSTANT OF GRAVITATION.

Experiment 8.

\[
\begin{align*}
\theta &= 65^\circ - 22' = 64^\circ 38' \quad \sin 64^\circ 38' = 0.9035847 \\
R_H &= R_r = 2.99304 \quad \cos 64^\circ 38' = 0.4284055 \\
v_H &= v_r = 449650 \\
\log r &= 1.6499673 \\
p &= R \sin \theta = 2.704465 \\
b_r &= R \cos \theta = 1.282247 \\
b - r &= 835597 \\
b + r &= 1.728897 \\
p^2 &= 7.314131 \\
(b - r)^2 &= 0.698222 \\
(b + r)^2 &= 2.989085 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>Low.</th>
<th>High.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h_H)</td>
<td>0.0321</td>
<td>0.002092</td>
</tr>
<tr>
<td>(H_H)</td>
<td>6.048339</td>
<td>36.582411</td>
</tr>
<tr>
<td>(H_H^2)</td>
<td>6.028855</td>
<td>36.347032</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\log D^2 &= 0.9038157 \quad \log D^2 &= 0.9039042 \\
\log D &= 0.4519078 \quad \log D &= 0.4519521 \\
\log D^3 &= 1.3557235 \quad \log D^3 &= 1.3558563 \\
\log p &= 0.4320814 \quad \log p &= 0.4320814 \\
\log p/D^3 &= 1.0763579 \quad \log p/D^3 &= 1.0762251 \\
\log M &= 3.8696634 \quad \log M &= 3.8696634 \\
\log m &= 0.4234097 \quad \log m &= 0.4234097 \\
\log r &= 1.6499673 \quad \log r &= 1.6499673 \\
\log q &= 3.013579 \quad \log q &= 3.0192721 \\
\log \text{couple} &= 3.013579 \quad \log \text{couple} &= 3.0192721 \\
\end{align*}
\]

\[
\begin{align*}
\text{Couple} &= 1045.580 \quad 1045.371 \quad 73.880 \quad 74.446 \\
&= 1045.371 \quad 74.446 \\
&= 2090.951 \quad 148.326 \\
\end{align*}
\]

\[
Q = 1042.625
\]

In order to determine the moments of the attractions of the large balls \(M, M\) upon the small ones \(m, m\), the distances represented in figure E by \(p\) and \(r\), and the true distances \(D\) between \(M, M\) and \(m, m\) are required, also the masses \(M, M\)

MDCCXCXV.——A.
Fig. E.

...and \( m, m \) — that of displaced air. Then the moments are for any one attraction out of the four possible,

\[
\frac{G M m p r}{D^3}
\]

These are most readily obtained from the observations in the manner set forth on the last page, where every figure made use of is set down. Single multiplications are performed on the arithmometer more quickly than by logarithms, hence natural sines and cosines are employed. Continued multiplications are more conveniently performed by logarithms, and the change from \( D^2 \) to \( D^3 \) can only be so effected.

The angle, \( \theta \), is the amount through which the lead balls are turned from the neutral position — the angle through which the gold balls are deflected.

\( R \), the radius of motion of either lead ball, is half the distance between the axes of the wires, and they are taken in the calculation as being identical, i.e., there is supposed to be no eccentricity. In Experiment 5 I calculated the result both on this supposition and more laboriously giving the true and slightly different values to \( R_L \) and \( R_L \), the radius of motion of the upper and of the lower ball respectively. The difference in the result only amounted to 3 parts in 2,000,000, and so, as I explained on p. 26, a small eccentricity, if it exists, is of no consequence.

\( r \), the radius of motion of either gold ball, is half the distance between the axes of the fibres. The next few lines explain themselves; they simply give intermediate quantities required for the solution of the different triangles. \( h_L \) and \( h_U \) are the differences of levels of the centres of the lower gold and lead balls and upper gold and lead balls respectively. \( H_L \) is the difference of level of the lower lead and upper gold ball and \( H_U \) the other great difference of level. The four couples obtained are those due to the attraction of the two pairs at the same level and of the two pairs at different levels. The latter are in the opposite direction to the former, and are therefore subtracted. The result, 1942.625, when multiplied by \( G \), is the actual moment produced upon the torsion fibre by the action of the balls upon one another.
upon the supposition that the balls are all spheres, and act as if they were concentrated in their centres. The brass ball holders, as already explained, cause the forces to be actually more than they appear to be, on the assumption that the lead balls act as if they were concentrated in their centres, so that \(1 + 0.001366\) is the factor by which the couple must be multiplied to correct for the brass ball holders. The corresponding correction for the gold ball holder is only \(\frac{1}{250000}\) of the whole. One small correction, too small to matter, but which I have calculated with some labour, is the stability due to the gravitation of the table. This introduces a restraining couple upon the balls alone in Experiment 8 of \(\frac{1}{263000}\) of the whole. Finally, there is the correction already mentioned on p. 31 of \(-\frac{1}{263000}\) on account of the attraction of the gold ball for the wires and the lead ball for the fibres. Combining all these, the actual couple developed is found to be equal in Experiment 8 to 1942.882 inch\(^2\) gramme
\[
\text{second}^2 \quad \text{units.}
\]

3. The Dynamics of the Moving System.

As before, I shall take my example from Experiment 8.

Moment of inertia of counterweight No. 3 or C. . . \(= 0.0163120\)

\[
T_b^2 \quad 37245.9 \quad \quad T_b^2 - T_c^2 = 35547.17
\]

\[
T_c^2 \quad 1698.73
\]

\(T_a^2\) not taken.

Moment of inertia added to beam when balls are placed in position, called B.

\[
B = \begin{cases} 
\text{balls translated} & 5.302804 \times 0.44665^2 \\
\text{+ hooks translated} & 0.1190 \times 0.379^2 \\
\text{+ balls rotated} & 4 \times 5.300252 \times 0.126134^2 \\
\text{+ hooks rotated} & 0.012 \times 0.025^2 
\end{cases}
\]

\[
B = 1.0933364 \quad C = 0.016312
\]

\[
B - C = 1.077024
\]

\[
U = \frac{BT_c^2 - CT_b^2}{T_b^2 - T_c^2} = 0.0351565,
\]

\[
S = \frac{4\pi^2 (B - C)}{T_b^2 - T_c^2} = 0.001196133.
\]
The moment of inertia of the counterweight is directly obtained from its dimensions. The moment of inertia added to the beam requires more explanation. When the balls are hung on to the beam in the manner already described, they add to its moment of inertia, both on account of their distance from the axis, and on account of their own moments of inertia, about their own axes. Besides the balls the small wire hooks and the quartz fibres produce their own effects. These are found in the four lines bracketed B. In the first line the mass of the balls is made up as follows:—

\[
\text{Mass of gold balls + wire holders, corrected for buoyancy as against brass weights, but not absolutely, } + \frac{1}{3} \text{ mass of displaced air. } \ldots \quad 5.302204
\]

\[
+ \text{ mass of quartz fibres. } \ldots \ldots \ldots \quad .00060
\]

\[
5.302804
\]

this is multiplied by the square of the radius \( r \).

In the second line the radius of the support of the hook is obtained by direct measurement of the beam itself. It is relatively unimportant. In the third line the mass of the balls does not include the ball-holders or fibres or (perhaps wrongly) that of any surrounding air. The radius of the ball is found by a screw micrometer. The fourth line needs no explanation; it is infinitesimal.

U is found from the formula placed next to it. This is the moment of inertia of the mirror. It is not required in the calculation, but is found for the purpose of comparison. It should be constant.

S represents the stiffness of the torsion fibre, \( i.e. \), the couple that must be applied in order to twist it through unit angle \( (57^\circ.296) \).

If the unknown moment of inertia had been eliminated by the usual method, that is by supposing the torsion constant while the mirror was made to swing either \( \text{with} \) or \( \text{without} \) a known added moment of inertia (in this case, that due to the balls) then \( T_B^2 \) and \( T_0^2 \) would have been required. Taking \( T_0^2 \) from the previous experiment when it was found to be 1168.00,

\[
U \text{ becomes } \frac{1T_B^2}{T_B^2 - T_0^2} = 0.035396
\]

and

\[
S \text{ becomes } \frac{4\pi^2B}{T_B^2 - T_0^2} = 0.001196375.
\]

Since the torsion is not the same when \( T_B^2 \) and \( T_0^2 \) are being found, as in one case the fibre is much more strongly stretched than in the other, and is therefore longer and thinner, and is not necessarily made of a material having the same rigidity, the above figures are spurious. They differ from the true figures found in the previous page, but U, which is eliminated differs far more than S, which is made use of. The
reason of this is made clear if a correction, \( \theta \) in terms of \( S \), is included in the expressions for \( U \) and \( S \). Since the fibre becomes stiffer when the balls are taken off, it is simpler to consider this correction as a stiffening of the fibre when it is unloaded instead of the reverse when it is loaded. The expressions are now:

\[
U = \frac{3T_0^2 (1 + \theta/S)}{T_b^2 - T_0^2 (1 + \theta/S)},
\]

\[
S = \frac{4\pi^2 B}{T_b^2 - T_0^2 (1 + \theta/S)}.
\]

It now appears that in both, the denominator is affected to the same extent, which is very small since \( T_0^2 \) is small compared with \( T_b^2 \). On the other hand the numerator of \( S \) is not affected, while the correction applies to the whole numerator of \( U \).

The very great effect of this upon the absolute value of \( S \) is well shown in Experiment 9, where the additional weight was 7.975 instead of 5.314 grms. In consequence of the extra amount of stretching \( S \) fell from 0.01196 to 0.01147, or nearly 5 per cent. The actual elongation of the torsion fibre in the two cases was 0.0394 and 0.0677 inch. The whole length of the fibre was 17 inches, so the amount of stretch was 232 and 398 per cent. Even if the volume of the fibre remained constant the diminution of torsional rigidity could not be accounted for with a material of constant rigidity. This point is perhaps worth considering in connection with Poisson's ratio and the theory of elasticity, more especially in consequence of the great hardness, freedom from structure and possible elongation without permanent deformation or change which are met with in a quartz fibre. I must, however, defer its discussion for the present or leave it to some one more competent than myself.

4. The Combination of the preceding Three Results.

The method of combining the results given in the first three sections of this part is simple enough. From the first section, the deflection in scale divisions when the lead balls are moved from the + to − positions is obtained. Let this be called \( P \). The second section gives \( Q \) the numerical coefficient of \( G \) ; thus, \( QG \) is the couple exerted upon the fibre. From the third section, the actual couple \( S \) that would be needed to twist the torsion fibre through an angle of 1 unit (57°.3) is obtained without any reference to \( G \), and \( D \) being the actual distance in units or tenths of a scale division from the scale to the mirror measured as explained on p. 17, it follows

\[
G = PS/4QD.
\]

The 4 in the denominator is due to the doubling of the angle by reflection and to the doubling of the deflection by moving the lead balls from the + to the − positions. \( G \) is thus obtained in inch²/gramme second² units; to convert it into
centimetre$^3$/gramme second$^2$ units it is merely necessary to multiply by 16.3861, the number of cubic centimetres in a cubic inch.

To obtain from this the density of the earth I might have recalculated the attraction of the earth treated as a rotating ellipsoid composed of similar shells of equal density as given in Professor Poynting's paper, but since it is obvious that $G\Delta$ is a constant, and is, taking Poynting's figures, equal to $36.7970 \times 10^{-8}$, it is merely necessary to divide this figure by $G$ to find $\Delta$.

Again, taking Experiment 8 to furnish an example, these operations are as follows:

$$G = \frac{PS}{4QD} = \frac{3695.4 \times .00119598}{4 \times 1942.882 \times 139965} = 4.06312 \times 10^{-6}$$

in inch$^3$/gramme second$^2$ units.

Multiply by 16.3861, then $G = 6.6579 \times 10^{-8}$ in C.G.S. units, and $\Delta = 5.5268$.

The more important quantities of the whole series of experiments are exhibited in Table I, which, as the heading shows, is constructed on the Inch, Gramme, Second system, in conformity with the actual measurements. The supplementary table is a repetition of the most important quantities in C.G.S. units. Here below the constant of gravitation $G$ is to be found the series of values of $\Delta$ the mean density of the earth. Appended are Cornu's and Poynting's values, Cornu's $G$ being obtained from his $\Delta$ in the same way that I obtained my $\Delta$ from my $G$.

An examination of the table shows that I have employed a fair variety of conditions, the lead balls alone being unchanged throughout the series. Three pairs of small masses were made use of. The lead balls were practically unchanged in distance, though, after Experiment 7, they were brought nearer together by $\frac{1}{50}$ inch about. The effect of this on the deflection $P$ and the couple $Q$ is at once evident in Experiment 8. Three fibres were employed, though, as already mentioned, the rigidity was very different in Experiment 9 owing to the great longitudinal strain. The different torsional rigidities are tabulated under $S$.

The periods are tabulated under their squares, i.e., after correction for damping. $T_3^2$ is with the gold balls or cylinder suspended from the mirror and with the lead balls at a + or − position, where, by producing a maximum couple, they do not affect the period. $T_9^2$ is the corresponding period with the lead balls in their neutral position where they accelerate the period. I might, following Reich, have independently calculated $G$ from the acceleration produced in this way, but these periods were not determined with the same care as the others, and in any case, the difference is too small for an equally accurate result to have been obtained. $T_3^2$ and $T_9^2$ are the square of the periods with counterweights and with nothing on the mirror.

The pairs of quantities tabulated under $H_L^H$ and $H_L^W$ are the four differences of levels between the lead and gold balls. Thus 6.0296 in Experiment 5 is the

* $3695.4 = 3696.4 - 1$. See p. 56.
+ $0.00119598 = 0.00119613 (1 - 1/7850)$. See p. 35.
### Table I.—Inch, Gramme, Seconds.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>7406:67</td>
<td>for all but No. 3 and 9</td>
<td>39816</td>
<td>39831</td>
<td>299273</td>
<td>299269</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>1:2988</td>
<td>2:6511</td>
<td>3:00420</td>
<td>3:00312</td>
<td>2:99304</td>
<td>2:99310</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>0:1</td>
<td>0:0059</td>
<td>0:00275</td>
<td>0:00275</td>
<td>0:0016</td>
<td>0:00790</td>
<td>0:0015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>3655:092</td>
<td>1168:00</td>
<td>3667:6</td>
<td>3664:0</td>
<td>3664:0</td>
<td>3695:4</td>
<td>3775:5</td>
<td>3515:4</td>
<td>3520:5</td>
<td>3520:5</td>
</tr>
</tbody>
</table>

### Centimetre, Gramme, Seconds.

<table>
<thead>
<tr>
<th>Q</th>
<th>6089:89</th>
<th>12423:8</th>
<th>12422:3</th>
<th>12432:8</th>
<th>12534:2</th>
<th>18800:5</th>
<th>12531:8</th>
<th>12533:7</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0:0245483</td>
<td>0:0772104</td>
<td>0:00119681</td>
<td>0:00119598</td>
<td>0:00114709</td>
<td>0:00125697</td>
<td>0:00125755</td>
<td>0:00125755</td>
</tr>
</tbody>
</table>

### Cornu.

<table>
<thead>
<tr>
<th>Summer mean.</th>
<th>Winter mean.</th>
<th>Set I., mean.</th>
<th>Set II., mean.</th>
</tr>
</thead>
<tbody>
<tr>
<td>G 10⁻⁸x</td>
<td>6:6181</td>
<td>6:6903</td>
<td>6:6661</td>
</tr>
<tr>
<td>Δ 10⁻⁸x</td>
<td>5:56</td>
<td>5:50</td>
<td>5:52</td>
</tr>
</tbody>
</table>

### Poynting.

<table>
<thead>
<tr>
<th>Set I., mean.</th>
<th>Set II., mean.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:6661</td>
<td>6:7393</td>
</tr>
</tbody>
</table>
difference of level of the upper lead and lower gold ball, while 6.0139 is the corresponding difference between the other pair. Similarly 0.0059 is the difference of level of the upper lead and upper gold balls, and 0.0216 the difference of level of the lower pair of balls.

In order to eliminate as far as possible any systematic errors that might arise for instance from imperfections of the copper central tube, which of course is very near the gold balls, or from want of perfection in the lead balls, though nothing comparable with the error of experiment need be feared on this account, I made some change in the circumstances after every experiment. Thus, after Experiments Nos. 1 and 2 had been carried out, which were merely preliminary so that I might learn something of the behaviour of the apparatus, I arranged the balls in Experiment 3 as follows:

- Lead ball, No. 1, Wall side, High level,
- , , , 2, Arch , Low 
- Gold , , 3, Wall , High 
- , , , 4, Arch , Low 
- Neutral reading of lid 267°.

The arch side is the right as seen from the telescope, or the left as seen from the back when the optical compass is in use. This expression depending upon the structure of the cellar avoids ambiguity.

The corresponding arrangement in the whole series of experiments with the dates at which they were carried out is given in Table II.

As would be expected, I had not at first all the details so complete as at the end of the series of experiments. Thus, in Experiment 3, the air drawing arrangement for steadying the mirror or starting it into motion, had not been thought of. At that time, for want of a better arrangement, I had to enter the corner and withdraw the back window, fig. 12, so as to allow the accidental movement of the air to start a swing of great amplitude. As I have already indicated, the decrement is, in spite of all I can do to prevent it, inconveniently high, so that periods extending over forty-five minutes cannot be taken unless the mirror has an oscillation of large amplitude at starting, far larger than two or three reversals of the lead balls in time with the oscillation would set up. The plan was essentially bad owing to temperature, disturbance, and tremor, nevertheless the observations made at the time were fairly consistent, thus two periods in the + position on October 16th, gave 241.93 and 241.90. The next day I put up the felt screens and two periods were 241.9(4) in the + position, and 241.88 in the negative. I then introduced a different method of producing a swing of great amplitude, viz., in the air tube then screwed into the back window, fig. 12, I fitted a glass stop-cock which could be turned on or off without touching the metal windows or screens. I did this hoping that a clockwork fan belonging to a lamp would produce a gentle draught upon the end of the mirror when set in action opposite a
<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>Lead balls</th>
<th>Position of shellae spots</th>
<th>Gold balls</th>
<th>Neutral lid reading</th>
<th>Date</th>
<th>Notes as to additions, alterations, or improvements</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>No. 2 low</td>
<td>No. 1 high Inwards (?)</td>
<td>No. 4 low</td>
<td>267</td>
<td>1892, Oct. 1 to Oct. 30</td>
<td>During this experiment put up the underfelt and eccentric metal screens</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 3 high</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Gold balls of double the weight.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>No. 2 low</td>
<td>No. 1 high Inwards</td>
<td>No. 4 low</td>
<td>267</td>
<td>1893, Aug. 15 to Sept. 3</td>
<td>First used soldered fibres</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 3 high</td>
<td></td>
<td></td>
<td>Amalgamated platinum pendulum point</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wafting abolished; replaced by drawing air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Unamalgamated platinum pendulum point</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Earthquake (Sept. 9)</td>
</tr>
<tr>
<td>5</td>
<td>No. 1 high</td>
<td>No. 2 low Inwards</td>
<td>No. 3 high</td>
<td>865</td>
<td>Sept. 4 to Sept. 11</td>
<td>Put up octagon house</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 4 low</td>
<td></td>
<td>Sept. 12 to Sept. 14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>6</td>
<td>No. 2 low</td>
<td>No. 1 high Inwards</td>
<td>No. 4 low</td>
<td>2659</td>
<td>Sept. 16 to Sept. 18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 3 high</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>No. 2 low</td>
<td>No. 1 high Outwards</td>
<td>No. 4 low</td>
<td>2659</td>
<td>Sept. 16 to Sept. 18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 3 high</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>No. 1 low</td>
<td>No. 2 high Inwards</td>
<td>No. 3 high</td>
<td>2659</td>
<td>Sept. 16 to Sept. 18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>May 21</td>
<td></td>
</tr>
<tr>
<td>(Cylinders.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>May 21</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>No. 1 low</td>
<td>No. 2 high Inwards</td>
<td>No. 3 low</td>
<td>86</td>
<td>Sept. 27 to Oct. 3</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 1 high</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>No. 1 low</td>
<td>No. 2 high Inwards</td>
<td>No. 4 low</td>
<td>8525</td>
<td>1894, Jan. 1 to Jan. 13</td>
<td>First put up the magnetic arrangement for recovering lost gold balls, &amp;c.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 3 high</td>
<td></td>
<td>May 21</td>
<td>(Hydrogen experiment)</td>
</tr>
<tr>
<td>11</td>
<td>No. 1 low</td>
<td>No. 2 high Inwards</td>
<td>No. 4 low</td>
<td>8525</td>
<td>Jan. 14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 3 high</td>
<td></td>
<td>Jan. 21</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>No. 2 high</td>
<td>No. 1 low Inwards</td>
<td>No. 3 high</td>
<td>2652</td>
<td>Jan. 17 to Jan. 21</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. 4 low</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
funnel-shaped end to the pipe. This did not work, and I was therefore compelled at the time to produce the draught by some ready means; gentle movement of a sheet of paper at a distance from the instrument produced the desired motion, but my going near the instrument at all was essentially bad. The periods obtained after this were:

<table>
<thead>
<tr>
<th>Date</th>
<th>Period</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct. 29</td>
<td>241.99</td>
<td>+</td>
</tr>
<tr>
<td>,</td>
<td>241.91</td>
<td>-</td>
</tr>
<tr>
<td>, 30</td>
<td>241.88</td>
<td>-</td>
</tr>
<tr>
<td>,</td>
<td>241.93</td>
<td>+</td>
</tr>
</tbody>
</table>

I noticed slight differences between periods taken with the lead balls in the + and − positions with my preliminary apparatus, but, though I am not able to explain it, I am glad to say that, with the more perfect setting and screening now in use, it has practically disappeared. The two periods taken with the counterweight gave identical results, 64.954 seconds.

The soldered fibres used in all the later experiments seem a definite improvement, as the creeping of the zero, which was never very troublesome, almost entirely ceased.

The traffic and the trains are not the only causes of disturbance. Wind, by pressing upon the building and neighbouring trees, of course shakes the ground; but on Sept. 9–10, a particularly quiet night, I had to leave, owing to a sudden disturbance producing a pendular motion of 15 divisions, or 150 units, and for some time there was no quiet. As the motion was clearly produced by a lurch of the whole instrument and table carrying it, and was greater in amount than any traffic in the busiest part of the day had ever produced, and was moreover free from the high period tremor characteristic of human disturbance, I at once set it down to an earthquake. I was marking transits of every 10 divisions at the time. The moment of the last mark was 15h. 44m. 14.3s., allowing for the error of the clock as determined at the Observatory. The next mark was due in 3 seconds, but I was, of course, unable to record it. In the 'Standard' of Sept. 12th there was an account of a violent earthquake at Jassy, which was felt also at Bucharest, at six o'clock in the morning. I have not ascertained the exact time at which the earthquake was felt in Roumania, or the amount to allow for difference of longitude, but these, no doubt, can be supplied from Vienna.*

Experiment 11 was a purely comparative one. Everything being left as in Experiment 10, a tube was connected with the stop-cock in the bell-jar J, and with a hydrogen bottle and drying bottle, so that dry hydrogen could be fed in to displace the air in the central tube. The object was to see if any advantage would be derived from the smaller viscosity of hydrogen; but, though the resistance fell so as to change

* Mr. Charles Davison informs me that the shock was recorded at Bucharest at 3h. 40m. 35s., a.m., but that the epicentrum must have been some distance from there. The time interval between Bucharest and Oxford appears very small, the usual rate of travel being 3 km. a second, or a little more.
the decrement from 0.842 to 0.937, which in itself was a great advantage, so much difficulty seemed inherent in the method that I determined not to prosecute it. The values found this night for $T_e^2$ were

\[
\begin{align*}
\text{In air} & \quad \ldots \quad 35404 \\
\text{In hydrogen} & \quad \ldots \quad 35401
\end{align*}
\]

The deflections owing to disturbance could not be so accurately determined as usual; they were

\[
\begin{align*}
\text{In air} & \quad \ldots \quad 3520 \\
\text{In hydrogen} & \quad \ldots \quad 3523
\end{align*}
\]

The only observation of real interest in connection with the hydrogen experiment was the effect of the gas upon the mirror. The mirror was bent to a small extent, causing the image of the divisions to practically disappear. A movement of the eyepiece outwards of about $\frac{5}{8}$ inch was needed to make them appear sharp again. On letting the gas escape the focus went back to its old place, and this was repeated without variation three or four times. I imagine that the glass became convex under the influence of the hydrogen in consequence of the glass being penetrated by the quickly-moving molecules, and so becoming expanded in the front or unprotected side, while the silver and lacquer at the back prevented this action, much as paper or lace will protect glass from the cutting action of a sand-blast. The bending may have been produced by a contraction of the lacquer or silver, but this seems hardly conceivable. An interesting line of inquiry is suggested by this experiment, but I have not been able to do more at present.

An examination of the results shows that they hover about two values, experiments 3, 4, 5, 6 and 12 being about 5.520 for $\Delta$, and the remainder about 5.528. It is impossible to trace any connection between the arrangement of the apparatus, &c., and this small irregularity. It is necessary, therefore, to review the deflections and periods of each and the conditions, whether of disturbance or quiet, under which they were carried out. No. 3 has already been discussed, and the wonder is that it should agree so well with the others when the imperfect conditions are borne in mind, and when it is remembered that the torsion fibre in this experiment had only one-third of the rigidity of those used later, while the gold balls were only half as heavy.

As already mentioned, the periods in Experiment 4 were lost, so that an absolute result could not be calculated. The values of $2\tau$ in the two cases only differed by 0.0002 inch, an amount which is probably beyond the certainty of measurement, and therefore the results for 4 are merely obtained from those from Experiment 5, by multiplying or dividing by the ratio of the deflections.

Deflections and periods for Experiment 4 were taken over several days. The deflections were:

\[ k = 2 \]
The mean of all but the one in brackets, which depends on a single value only, is 3668.1. The deflection for Experiment 5 is 3668.6, practically an identical quantity, so that the G and \( \Delta \) of the two are almost the same. The two results should properly be considered as one. Both unfortunately depend upon unsatisfactory period observations which, when squared, varied from 37200 to 37240. On this account the results from Experiments 4 and 5, which are higher than any of the others for G and lower for \( \Delta \), should have had a bad mark put against them. In Experiment 6 the deflections were nearly as consistent as those in Experiment 4, while the periods were now nearly the same in the + and − positions, being, when squared, 37245 in the − and 37247 in the + positions. The conditions of this experiment seemed decidedly favourable, and I see no reason inherent in the observations that could lead me to doubt the accuracy of the results.

In Experiment 7 the only change was twisting the lead balls so that the sides that were inwards should be outwards. The sudden change in the result for \( \Delta \) from 5.5189 to 5.5291 might seem to be due to some irregularity of density in the lead balls. But the extraordinary agreement between this result and the three following, where every kind of change was made in the conditions, including the turning of the balls again, and the change from high to low and low to high, and where, moreover, the extra steadiness of temperature due to the screening of the octagon house was introduced, shows that this argument will not hold. I cannot account for this small difference. In Experiment 8 all the conditions were most perfect. The figures for this have already been given, and so need not be repeated. I may, however, compare the squares of the periods of Experiments 6, 7, and 8, throughout which the beam mirror and gold balls were never touched, to show how much better the agreement was at this time than before.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Date</th>
<th>− position</th>
<th>+ position</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Sept. 14</td>
<td>37245</td>
<td>37247-5</td>
</tr>
<tr>
<td>7</td>
<td>&quot; 15</td>
<td>&quot;</td>
<td>37242</td>
</tr>
<tr>
<td>8</td>
<td>&quot; 17</td>
<td>&quot;</td>
<td>37245-9</td>
</tr>
</tbody>
</table>

The last figure of this series was taken in determining S. I may mention that a
change of $\frac{3}{10}$ inch in $2R$ was made in this experiment, the effect of which is at once evident both in $P$ the deflection, and in $Q$ the geometrical factor.

In Experiment 9, the conditions were completely changed by the substitution of gold cylinders for gold balls. As already mentioned, the torsional rigidity of the fibre was altered 5 per cent. by the great tensile strain, yet with every quantity redetermined the only change in the result was about 1 part in 1500. The old conditions were realised again in Experiment 10, except that I had taken the fibre to London, re-soldered the broken ends and waited three months, but the result only differed from that of Experiment 8, by 1 part in 60,000. Perfect conditions were met with again, the mean deflections for the two nights, January 6 and January 7, being 3516.5 and 3516.3. The last experiment on January 21 was disturbed, and the points of rest varied several units in the course of the night. I was compelled, moreover, on leaving the apparatus at 17th, to take off the gold balls, replace them by the counter-weights, and after about three hours’ sleep, to return again and take the counter-weight period. This was far too soon for the temperature to have settled after disturbance, and in addition to this cause of error, I had only 10 minutes in which to take the period, and had then to hurry off with the drum record still wet, in order to be in London where I had to lecture at noon. I cannot, therefore, look upon this experiment with the same confidence as Nos. 7 and 10, and so with the exception of Experiment 6, all those that give the lower value for $\Delta$ have something against them. Under these circumstances, I cannot do otherwise than look to Experiments 7, 8, 9, and 10 as being the most likely to give a true value. Moreover, as Nos. 8 and 10 were both made under most favourable yet very different conditions, their closely agreeing figures carry more weight than the other two. I therefore conclude that $\Delta = 5.5270$ and $G = 6.6576 \times 10^{-8}$. The fifth figure in such case is, of course, a purely arithmetical phenomenon, but I do not think that the fourth figure can be more than 1, or at the outside 2 in error.

I had hoped to have made a greater number of experiments under more widely differing conditions, but the strain which they entail is too severe, for not only have I had to give up holidays for the last three years, but to leave London on Saturdays and occasionally to sit up all Saturday and Sunday nights at the end of a week’s work. The conditions, therefore, are too difficult for such an extended series as I should like to make to be possible, and I must after one more effort, leave the problem to others who have leisure, and what is of far greater consequence, a quiet country place undisturbed by road and railway traffic, and who possess the knowledge and manipulative skill which the experiment requires.

Conclusion.

I think it might be useful, now that the autumn has passed and I have been unable to make a new series of observations, if I were to state my views as to any change of
detail that might conduce to greater accuracy. I am still convinced that G may be
determined with an accuracy of 1 in 10,000 by means of apparatus such as I have
described.

In the general design I am unable to suggest any improvement. The weakest spot
is caused by the resistance of the air making time work difficult, especially where
visible shaking interferes with the usefulness of oscillations of small amplitude. I
doubt if a practical gain is to be obtained by the use of hydrogen, and I am sure that
a high vacuum is out of the question. The only remedy, therefore, is to employ
larger suspended balls, and with them a longer beam. For the same argument that
shows that with any length of beam the limit of sensibility imposed by the strength
of the fibre is increased by reducing the weight of the suspended balls, for the rigidity
of a fibre varies nearly as the square of its strength, shows also that if the fibres are
not far from their breaking weight, the size of the balls cannot be increased without
reducing the sensibility. But increase of size would be advantageous because, while
the forces depend upon the cube of the diameter, the resistance to movement depends
upon the square. The result is a less serious decrement with larger balls. Now, in
order to employ these and yet maintain the period with the necessarily stronger
fibre, a longer beam must be employed. Of course, unless the diameter of the large
attracting balls are increased in the same proportion the angle of deflection will fall.
I do not think that the beam needs to be lengthened to more than about two
inches. If this length were adopted it would be better to aim at 5 centims., for since
this is half a decimetre, a more accurate determination of the length could be obtained
by reference to the standard decimetre at Sèvres, than would be possible if it were not
very nearly an exact submultiple. Whether or not the lead balls and the whole
apparatus should be doubled in size is a mere question of cost. The expenses
would run up very rapidly with very moderate increase of sensibility. I should feel
disposed to be content with lead balls about six inches in diameter, but I would
certainly have an Elmore tube for the centre one T, and, by preference, for the large
cylinder C. The slight diminution of angular deflection which would result from this
change, would be more than compensated by the doubled optical definition, but there
might be some difficulty in obtaining a thin rectangular mirror 5 \times 1 centims., in
which no optical defect could be detected.

It may appear that I am reversing all my arguments and practice in now advocating
an increase of size, but it must be remembered that the object is not so much to
increase the sensibility, or even to be able to make better geometrical determinations,
for both of these, in my apparatus, exceed the square of the periods in the degree of
accuracy with which they are known. The object is solely to be less influenced by
the viscosity of the air, but this would not have limited the accuracy of my periods so
seriously if I had not been disturbed by trains.

I should have had less confidence in this doubling of the size, if my supposition
that the disturbing moments, due to convection, were proportional to the seventh
power of the linear dimensions, had been correct. Since it varies only as the fifth power, and the quietness of the air is so great in my apparatus (p. 11), there can be no objection on this account to the double size; but I would strongly urge that in such a case, a room more uniform in temperature than the one at Oxford should be employed. It would also be well to lay non-connecting mats on those parts of instruments on which the hands are apt to rest when the balls are being transferred, or other manipulative operations are being carried out, so as to reduce, as far as possible, access of heat, and hence the interval that must elapse before observations of deflections or periods can be undertaken. I do not think any ready-made room is likely to be found available. A disused adit, at a great distance from existent mining operations, would be perfect, if it could be made use of. The instrument could then be walled up in a room to itself, and the heat from the observer and the travelling lamp excluded far more perfectly than in my case. An adit would be convenient also, in that it would allow of the use of a greater distance from the scale to the mirror than could be obtained in an ordinary room. This should not be less than 20 metres.

I should recommend a slight change in the upper end of the lid pillars with the object of giving the ball holder two adjustments, one radially, and one at right angles to a radius, so that eccentricities observed by the microscope of the optical compass could be corrected.

I also think more pains should be taken with the beam mirror to insure its rotating about its own centre of gravity, both when the gold balls and when the counter-weight are suspended. This would remove any doubt as to its constancy of movement of inertia when made to oscillate under the three conditions, and would at the same time make observable eccentricity of the gold balls impossible.

Finally, I have suffered much from the great loss of time that results from the accidental fall of a gold ball down the central tube. It can only be replaced after lifting out the torsion head, torsion fibre, and beam mirror, so that all the centering adjustments are lost, besides which, there is the serious risk of breaking the torsion fibre whenever this operation is carried out. I would make the lower end of the central tube funnel-shaped inside, and employ a much larger holding down screw, with a central hole more than large enough to allow the gold ball to escape through it. This could, of course, be plugged at other times. In order to put the gold balls into their places without removing the torsion fibre, I would have a large hole in the torsion head behind (away from the big telescope) the torsion rod, and this would be easy with the larger central tube. Then if a special overhead wheel were placed with its edge vertically over the centre of this hole, the gold ball could be let down as described in the paper and transferred, as usual, on to one of the side hooks by the use of a simple tool made of a bent pin.

In every other respect the apparatus behaves so perfectly, and the operations are conducted with such facility, that I am unable to offer any other useful suggestion.
ON THE NEWTONIAN CONSTANT OF GRAVITATION.

Description of Plates 1 and 2.

PLATE 1.

Fig. 1 is a vertical section, and fig. 2 a sectional plan of the apparatus. Fig. 3 is a front view of a portion of it. Figs. 4, 5, 6 show details of the lid, pillars, and ball-holders on a larger scale. Fig. 7 represents the beam-mirror, counterweight, and eye-hooks full size. Figs. 8 to 10 show the window apertures in the central tube, beam raiser, &c., on a larger scale. Figs. 11 and 12 are the front and back windows used when deflections and periods are being observed. Figs. 13 and 14 show the back window for use with the optical compass. Fig. 15 represents the tubular screens; figs. 16 and 17, the mould for pressing the 4½-inch lead balls.

PLATE 2.

Figs. 18, 19, 20, and 21 are plan, side, and end elevations of the cellar with the apparatus in position. Fig. 22 is a horizontal section of the octagon house, the position of the apparatus being shown in dotted lines. Fig. 23 is an isometric projection of the geometrical clamps holding the scale and dummy. Figs. 24, 25, 26 are plan, front and side views, of the rotating and focussing slides and scale of the optical compass in position on the lid of the instrument, which is represented in chain lines. Figs. 27, 28, 29 are plan, front and side views, of the traversing slides and microscopes of the optical compass in position on the focussing slide, which is represented in chain lines.

Scale of Figs. Plates 1 and 2.

<table>
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<th>Scale</th>
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<th>1/3</th>
<th>1</th>
<th>1/2 inch to foot</th>
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<tr>
<td></td>
<td>14</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
II. On the Photographic Spectrum of the Great Nebula in Orion.

By J. Norman Lockyer, C.B., F.R.S.

Received June 13,—Read June 21, 1894.

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I. Description of the Photographs.

In February, 1890, I communicated to the Royal Society a preliminary note on some photographs of the spectrum of the Orion Nebula, taken at Westgate-on-Sea.*

The detailed discussion of the photographs has been reserved with the hope of securing others, but owing to other pressing work no further photographs have been obtained.

As the photographs in question show a greater number of lines than others which have been described, and especially as they appear to have an important bearing on the study of certain types of stellar spectra, I have thought it desirable that the publication of the results should no longer be delayed.

The instrument employed was the thirty-inch reflector, and a spectroscope by Hilger, having one prism of 60° and two half-prisms of 30°.

Mawson's instantaneous plates were used. The exposures were carried up to four hours, and five photographs were taken, some of them with shorter exposures than that named, in consequence of the sky becoming clouded or irregularities in the driving

clock, which was not then completely finished. One plate was exposed for four hours, on February 11, 1890, but, unfortunately, in consequence of the high wind, the slit was covered for an unknown part of this time by the velvet used to keep out stray light, and this was not at once discovered, as the finder for directing the telescope is at the lower end of the reflector tube, away from the spectroscope. This photograph only shows three or four of the more prominent lines, but they are all sharply defined. The other photographs were taken on February 2, 8, 9, and 10, the last with an exposure of three hours.

As a collimator has not yet been fitted to the tube of the reflector, the exposure of the plate to the flame of burning magnesium was made by closing the mirror cover, and burning magnesium at its exact centre. One half of the slit was exposed to the nebula, and the other half to the burning magnesium.

The part of the nebula photographed was the bright portion in the region of the trapezium. In some photographs, in consequence of clock irregularities, the stars of the trapezium have imprinted their spectra upon the plates, but these in no way interfere with the spectrum of the nebula, since a longish slit was used, and the spectra of the stars are narrow.

There is a remarkable and almost absolute similarity between the photographs obtained. The best one, taken on February 10, shows all the lines of the other photographs with others in addition, and this has therefore been selected for the determination of wave-lengths.

The probable mean position of the slit during the three hours' exposure of this photograph is shown in fig. 1, but the irregularities in the driving caused all the stars in the trapezium to cross the slit at different times.

![Fig. 1. Showing mean position of slit in photograph of February 10, 1890.](image)

It has not been found possible to reproduce the negative with advantage in consequence of its small size, but fig. 3 (see p. 80) gives a good idea of the appearance of the eleven principal lines shown in the photograph, and the position of the stellar spectra on the plate. Further reference to this diagram will be made later.

The principal lines are the three ordinarily seen in the visible spectrum, the lines of
hydrogen at $H_{\alpha}$, $H_{\beta}$, $H_{\gamma}$, and $H_{\delta}$, and the strong line in the ultra-violet near $\lambda 373$. $H_{\gamma}$ is by far the strongest line in the spectrum. The wave-length of the least refrangible line on the photograph was taken as 5006.5, as determined at Kensington, and this, together with the hydrogen lines, the line at $\lambda 4471$, and the ultra-violet magnesium triplet in the comparison spectrum, formed the basis of the curve for determining the positions of the fainter lines. The photograph was measured with a micrometer reading to 0.00001 inch.

All the lines are shown in the table which follows. In all, fifty-four lines have been recorded, and, of these, about twenty are seen without difficulty. The remainder require a favourable light, but no line has been inserted in the table which has not been measured several times by two observers. The spectrum extends from the ultra-violet to the green, and the intensities of the lines on the photographs naturally do not correspond to the visual ones; the F line, for instance, appears stronger than the brightest line in the visible spectrum at $\lambda 5006$. The photographic intensities are recorded in the table, six representing the strongest and one the feeblest line.

Some of the wave-lengths referred to in the preliminary paper have been slightly changed by the new reduction.
II. Table of Wave-lengths.

Table I.—Lines Photographed in the Spectrum of the Orion Nebula, Feb. 10, 1890.

<table>
<thead>
<tr>
<th>Micrometer reading.</th>
<th>Wave-length</th>
<th>Photographic intensity</th>
<th>Probable origin.</th>
<th>Wave-length of probable origins</th>
<th>Remarks</th>
</tr>
</thead>
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<td>3.3672</td>
<td>3707</td>
<td>2</td>
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III. The Origins of the Lines.

It will be seen from the table, that hydrogen enters largely into the composition of the vapours of the nebula. \( H_\beta, H_\gamma, H_\delta, H_\lambda, \) and the ultra-violet series, certainly as far as \( H_\lambda \) (new notation),\(^*\) are all present.

It is worthy of remark, however, that while, as previously stated, \( H_\lambda \) is the strongest line in the whole spectrum, and \( H_\beta, H_\gamma, \) and \( H_\lambda \) are also strong, the ultra-violet hydrogen lines are amongst the weakest.

Next to \( H_\lambda \), the line \( \lambda 373 \) is the most intense. In 1887, I suggested that this line was one of the members of the triplet seen in the spectrum of burning magnesium. As I stated in a preliminary communication, the wave-length could not be finally determined from the photographs already obtained, but it was probably near \( \lambda 3729 \).

This value, however, will require correction for motion in the line of sight. If Mr. Keeler's values\(^\dagger\) for the motion be accepted, and the earth's orbital velocity be allowed for, the correction will be about 0.22 tenth metres towards the red. This will bring the nebular line slightly nearer the least refrangible member of the magnesium triplet. Further measures of photographs taken with higher dispersion are necessary in order to settle this point.

The lines next in importance to those already mentioned, are near wave-lengths 4471, 4495 and 3868. The first of these, the strongest between \( H_\beta \) and \( H_\gamma \), is probably the line observed by Dr. Copeland in 1886. With reference to this line, I wrote as follows in a paper communicated to the Royal Society on Nov. 9, 1889.\(^\ddagger\)

"The observations of Dr. Copeland have now, I think, established the identity of the yellow line, in the nebula of Orion at all events with \( D_3 \). In a letter to Dr. Copeland, I suggested that the line at \( \lambda 447 \) was, in all probability, Lorenzoni's \( f \) of the chromosphere spectrum, seeing that it was associated both in the nebula and chromosphere with hydrogen and \( D_3 \). This he believes to be very probable. The line makes its appearance in the chromosphere spectrum about 75 times to 100 appearances of \( D_3 \), or the lines of hydrogen."

For the other strong lines near \( \lambda 3868 \) and \( \lambda 4495 \), no origins have been found.

From the final reduction of the photographs, as given in the table, it appears that the line formerly said\(^\S\) to be "near \( \lambda 4027 \)," is at \( \lambda 4025 \). It can, therefore, no longer be attributed to manganese. Its origin is at present unknown, but, as will appear later, it is a line frequently met with in the spectra of other celestial bodies. The line at \( \lambda 4690 \) referred to above, does not appear in the revised list, which only contains lines measured without great difficulty. Further, only a small proportion of the lines now mapped can be ascribed to metallic origins, but these, it will be seen, are

\(^*\) Vogel, 'Ast. Nach.,' 3198, 1893.
\(^\dagger\) 'Roy. Soc. Proc.,' vol. 49, p. 400, 1891.
\(^\ddagger\) Ibid., vol. 47, p. 30.
\(^\S\) Ibid., vol. 48, p. 200.
the chief lines in the spectra of the elements concerned. The table shows that a large number of the lines appear to have no terrestrial equivalent, but they are present in the spectra of other celestial bodies. These coincidences are discussed in a subsequent part of the paper.

IV. THE VARIATION OF THE SPECTRUM IN DIFFERENT REGIONS OF THE NEBULA.

The earlier investigations of the photographic spectrum of the Orion Nebula seemed to indicate that the spectrum was different for different regions.

In my own observations in 1891, with the 30-inch reflector at Westgate, the variations were very striking.

I stated in a paper communicated to the Royal Society in December, 1889,* "I obtained momentary glimpses of many bright lines between H₂ and H₂, on October 31." These were also seen by Mr. Fowler, and it was observed that, as the nebula was swept across the slit, in some parts the lines were seen together, while in other parts first one group and then another made their appearance. In the same paper I referred also to the variations in the same field of view of some of the lines. These observations were made with an enlarged form of pocket spectroscope, with a dispersion that does not split D. I found that in certain parts of the nebula, in the same field, certain lines were knotted, as often seen in prominences on and off the sun, and in other parts broken; in the former case, whilst the F line thickened equally on both sides, the chief nebular line thickened only on the more refrangible side.†

This result is shown in fig. 2.

† In another paper ('Phil. Trans.,' A, 1893, vol. 184, p. 714), I wrote as follows with regard to the chief line: "I have convinced myself of the fluted nature of the line by new observations made with instruments best fitted to show it, while the Lick telescope is, perhaps, the ideal telescope not to employ in such an inquiry. Hence, although the visibility of magnesium is not fundamental for my argument, I still hold that it is more probably the origin of the nebular line than an unknown form of nitrogen." The recent remarks of Professor Keeler ('Ast. and Ast. Phys.,' January, 1894, p. 61), and Mr. Campbell ('Ast. and Ast. Phys.,' May, 1894, p. 385), as to the relative efficiency of telescopes in regard to the observation of spectrum lines, seem to indicate that the matter has not been sufficiently thought out. I have not seen a statement as to the percentage of light utilised in the case of the Lick telescope, but I may say that at the time my observations were made, the mirrors of my telescope were newly-silvered, so that probably only a small percentage of light was lost. Neglecting the loss of light due to absorption in the case of the refractor, and to reflection in the case of the reflector, the brightness of the image formed on the slit of the spectroscope by the Westgate telescope is about sixteen times that of the image formed by the Lick telescope, and it is scarcely necessary to add that having this great illuminating power, the collimator of the spectroscope has been designed to take full advantage of it. [Professor Campbell, who has succeeded Professor Keeler at the Lick Observatory, is of the same opinion as myself. He writes ('Ast. and Ast.-Phys.,' 1893, p. 53): "The 36-inch telescope presents several positive disadvantages. . . . The ratio of the focal length 19:1 is much larger than exists in small telescopes, and hence the latter would form much brighter images on the slit plate." Note added 4.1.95.]
This was confirmed by Messrs. Fowler and Baxandall at Kensington, with the 10-inch equatorial, on October 31 and November 1, and again by Mr. Fowler with the 30-inch on November 2.

Fig. 2. Difference in the appearance of the lines at 4862 (F) and 5006.5.

It is also recorded in the Observatory note-book that at times these lines appeared of unequal length, the spectroscope employed in the observations having a long slit, and that sometimes 500 and 495 were seen without Hα. In the photographic investigation of variations in the spectrum, the question is complicated by differences in sensitive films, and in the case of a silver-on-glass reflector by the conditions of the mirrors. My own experience has shown that when mirrors are tarnished, the ultra-violet portion of the spectrum is weakened in greater proportion than the violet and blue.

One of the most striking variations previously recorded is that of the strong line in the ultra-violet near λ 373. This was the strongest line in the photograph taken by Dr. Huggins in March, 1882,* but it was not shown in Dr. Draper's photograph taken in the same year.†

Dr. Draper says: "I have not found the line at 3730, of which he (Dr. Huggins) speaks, though I have other lines which he does not appear to have photographed. This may be due to the fact that he had placed his slit on a different region of the nebula, or to his employment of a reflector and Iceland spar prism, or to the use of a different sensitive preparation. Nevertheless, my reference spectrum extends beyond the region in question."

A later photograph (1889), taken by Dr. Huggins,‡ did not show the line in question, the slit being placed on a different part of the nebula. As already stated, the line is one of the strongest in my photographs, though it is not quite as strong as Hγ. The spectrum photographed by Dr. Huggins, in 1889, differed entirely from those photographed by him in 1882 and 1888, the slit being again placed on a different region of the nebula.

My own photographs are specially interesting, as they indicate differences even in the small area of the nebula which is covered by the slit during a single exposure.

Some of the more important variations are indicated in fig. 3. The stars, the spectra of which are registered on the plate, will be readily identified by a comparison of figs. 1 and 3, the spectra of the trapezium stars being shown at the bottom of the diagram, and that of the star G. P. Bond 685 (Herschel's e) at the top.

It will be seen, for example, that the line near \( \lambda 495 \) falls off in intensity about the middle of its length, while the lines of hydrogen show no such reduction in the same part of the nebula. If we first consider the phenomena, in the neighbourhood of the star G. P. Bond 685 (Herschel's e), near the trapezium, it will be seen that here the lines 4471 and 4495 are most intense. In this region there is also a distortion of the two lines at 4471 and 4495; they are sharply bent towards the red end of the spectrum, whilst the other lines remain straight. Unfortunately, the spectrum of this star is only shown on the photograph of February 10, and, in the absence of other photographs, it is possible that the displacement of the two lines in question may be due to a distortion of the gelatine film. The displacement of the lines, if real, would indicate a velocity of about 200 miles per second, in the line of sight. Both lines are brightest where they are most disturbed.

![Diagram showing the principal lines in the photograph of the spectrum of the Orion nebula, February 10, 1890, with their relative intensities. The spectra of the stars in the trapezium are shown at the bottom of the diagram, while that at the top is the spectrum of the star Bond 685.](image)

It will be seen, also, that where the lines of the nebula cross the continuous spectrum of the star, they are considerably broadened. This is seen in all the principal lines from \( \lambda 373 \) to \( \lambda 495 \).

Where the chief line (500) crosses the spectrum of the star, there is a decided indication of a reversal. As it approaches the star, the line bifurcates and reunites on the other side, leaving a short dark line where it crosses the spectrum of the star, as shown in fig. 3. This reversal is not seen in the case of the hydrogen lines, but if it be subsequently confirmed in the case of 500, it will be an indication that some of the nebulous matter lies in front of the star in question (Bond 685; Herschel e).
SPECTRUM OF THE GREAT NEBULA IN ORION.

Coming now to the region of the nebula about the stars of the trapezium, it will be seen from fig. 3 that the bright lines are considerably widened where they intersect the spectra of the trapezium stars. In this case the hydrogen line at λ 4340 is widened very little on the less refrangible side, while, on the more refrangible side, the widening is nearly as great as its own breadth. Further, on each side of the line there is a decided break in the continuous spectrum of the stars, giving the appearance of a broad absorption band, with the bright hydrogen line running through it. This appearance is almost exactly reproduced at H₂.

Dr. Draper* appears to have noticed a peculiarity in the hydrogen lines where they crossed the spectra of the trapezium stars in his photographs of 1882. He says:—

"The hydrogen line near G, wave-length 4340, is strong and sharply defined; that at h, wave-length, 4101, is more delicate; and there are faint traces of other lines in the violet. Among these lines there is one point of difference, especially well shown in a photograph where the slit was placed in a north and south direction across the trapezium; the Hγ line, λ 4340, is of the same length as the slit, and, where it intersects the spectrum of the trapezium stars, a duplication of effect is noticed. If this is not due to flickering motion in the atmosphere, it would indicate that hydrogen gas was present even between the eye and the trapezium.

"I think the same is true of the H₂ line, λ 4101."

The line at 500 is only feebly impressed in the neighbourhood of the trapezium stars, and no reversal is visible.

It is clear, therefore, that the spectrum of the nebula varies very considerably in different regions.

V. DISCUSSION OF RESULTS IN RELATION TO THE METEORITIC HYPOTHESIS.

In my paper, "On the Photographic Spectra of some of the Brighter Stars," communicated to the Royal Society in November, 1892,† I made reference to the spectra of nebulae in relation to the meteoritic hypothesis. The statements were based upon an incomplete reduction of the photographs of the spectrum of the Orion nebula, and I now proceed to show how the hypothesis bears the test when the final reductions are considered.

On the hypothesis:—

(a) The normal spectrum of the nebula, including planetary nebulae, should have a complex origin.

(b) The bright-line stars are simply nebulae further condensed.

(c) With further condensation a group of stars of increasing temperature, with spectra consisting of mixed bright and dark flutings, is produced.

(d) Still further condensation results in a group of stars of increasing temperature, with spectra of dark lines, differing from the solar spectrum.

† 'Phil. Trans.,' A, 1893, vol. 184, p. 713.
(a) *The Complex Origin of the Spectra of the Nebulae.*

As pointed out in the paper referred to, the bright lines should have three origins, namely:

1. Non-condensable gases driven out of the meteorites.
2. Low temperature vapours produced by a large number of feeble collisions.
3. High temperature vapours produced by a small number of end-on collisions.

It will be seen from the tables that the requirements of the hypothesis in this respect are fully satisfied.

The lines of hydrogen and the flutings of carbon are what we should expect from the large interspaces; the flutings of magnesium and the low temperature lines of iron and calcium bring us face to face with phenomena connected with low temperatures, and they may be ascribed to the partial collisions; while the lines coincident with chromospheric lines must be regarded as high temperature products, since the solar chromosphere may be taken as indicating the spectrum we might expect to be associated with the high temperature vapours produced by the end-on collisions.

The undoubted presence of the lines D₂ and λ4471 left but little doubt as to the chromospheric relationship of some of the lines in the nebular spectrum, but the flood of new light thrown by the photographs taken with the prismatic cameras during the total eclipse of the sun on April 16th, 1893, put the matter beyond all question.

The discussion of the eclipse photographs will form the subject of a separate communication, but it may be here stated that the spectrum of the nebula shows a number of coincidences with lines seen in the spectrum of the chromosphere and prominences.


(b) *The Passage to the Bright-Line Stars.*

The association of the nebulae with the bright-line stars in the classification of the heavenly bodies was, I think, first suggested by me in 1887.*

So far as the planetary nebulae are concerned, this grouping has been abundantly confirmed by Professor Pickering's work on the bright-line stars, and by the visual observations of Professor Keeler.

Professor Pickering† tabulates the lines, and concludes with the statement that, "Owing to the similarity of the spectra of the planetary nebulae and the bright-line stars, they may be conveniently united in a fifth type." It is clear then, that in this particular, Professor Pickering accepts my proposed classification.

Mr. Keeler writes,‡ "The spectra of the nuclei of the planetary nebulae have a remarkable resemblance to the Wolf-Rayet and other bright-line stars, and an

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† 'Ast. Nach.,' 3025, 1891.
intimate connection between these objects, if established by further observations, would place the bright-line stars first in the order of development. The D₃ line appears in the central condensation of a number of bright nebulae, and with sufficient light would probably be seen in many of them, and this line is also predominant in most of the bright-line stars."

One of the main points of this paper is to show that the relationship indicated between the planetary nebulae and bright-line stars also holds good for such a nebula as that of Orion.

The bright lines seen in the visual spectra of the two classes of nebulae have long been known to be identical, and a comparison of the Westgate photographs with the results obtained by Professor Pickering, and the more recent work of Gothard,* and of Professor Campbell, at the Lick Observatory, on the spectra of the planetary nebulae,† has shown that the similarity also extends to the photographic region.

The fact that some of the nebular lines were apparently coincident with lines in the bright-line stars, was recognized at an early stage in the reduction of the Westgate photographs, and in the preliminary note I wrote as follows: "It is a very striking fact that some of the chief lines are apparently coincident, although the statement is made with reserve, with the chief bright lines in P Cygni, a magnificent photograph of which I owe to the kindness of Professor Pickering; it is one of the Henry Draper Memorial photographs."

The bright lines here referred to were those of hydrogen, and lines at 4025 and 4471. All these have since been photographed at Kensington, in the spectrum of P Cygni, and there is no longer any doubt as to their identity with bright lines in the nebula. Additional bright lines in the spectrum of P Cygni, photographed at Kensington, are also seen in the nebula, as shown in the following table:

| Table II.—Comparison of Orion Nebula with P Cygni. |
|-------------------------------|-------------------------------|
| Orion nebula. | P Cygni (Kensington). |
| 3968 | 3968 Hₓ |
| 4025 | 4015 |
| 4035 | 4035 |
| 4101 | 4101 Hₓ |
| 4147 | 4147 |
| 4340 | 4340 Hₓ |
| 4471 | 4471 |
| 4715 | 4715 |
| 4810 | 4810 |
| 4861 Hᵧ | 4861 Hᵧ |
| 4923 | 4923 |

† Ibid., p. 276.
Table III. shows in a complete form the details of the coincidences of the lines in the spectrum of the Westgate photograph of the Orion nebula with those of planetary nebulae and bright-line stars, as given by Pickering and Campbell. Only those lines of the nebula which show coincidences are included in this table, but the spectra of the planetary nebulae and bright-line stars are tabulated in full.*

It will be seen that all the lines of the planetary nebula, photographed by Pickering, appear in the Orion nebula, while of the twenty lines photographed by Campbell, twelve are present. Of fifteen lines in the spectra of the bright-line stars, eleven appear in the nebula.

Table III.—Comparison of Orion Nebula with Planetary Nebulae and Bright-line Stars.

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<th>Planetary nebula. (Pickering.) (Rowland's Scale.)</th>
<th>Planetary nebula. (Pickering.)</th>
<th>Bright-line stars, Type I. (Pickering.)</th>
<th>Bright-line stars, Type II. (Pickering.)</th>
<th>Bright-line stars, Type III. (Pickering.)</th>
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<td>5007</td>
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* Professor Pickering has been good enough to furnish me with glass copies of his beautiful photographs of the spectra of some of the bright-line stars. The positions of the various lines which he gives are in the main confirmed by the new measures which have been made at Kensington. I am in communication with him as to additional lines which have been mapped.

[In consequence of the delay in printing this paper, I am enabled to state that Professor Campbell has communicated some most important observations to 'Astr. and Ast.-Phys.,' 1894, p. 448, on the Wolf-Rayet stars, which show that the number of coincidences with lines in the nebula of Orion and planetary nebulae is increased by 7.—Note added 4.1.95.]
(c) Relation to Stars of Groups II. and III.

With further condensation, the interspaces between the meteorites will be reduced, and the bright-line stars will pass to stars with absorption spectra in which the dark lines correspond with the bright lines of the nebulae. There will, however, be intermediate stages (Group II. and the early stages of Group III.), as I have already pointed out.* At these stages, some of the high-temperature lines do not appear either as bright or dark lines, and this, no doubt, for the reason that the radiation from the interspaces is masked by the absorption of the vapours in the immediate neighbourhood of the meteoritic stones. In these stars the hydrogen lines are normally feeble dark lines, but the amount of radiating area in a cross section is so nearly equal to the amount of absorbing area that disturbances which, according to the meteoritic hypothesis, produce the increase of light in the variable stars of the group, are sufficient to make the hydrogen lines appear bright.

When we pass to the more condensed bodies, we find a group of stars, of which $\gamma$ Cygni is a typical case, in which the dark lines are very numerous,† but different from those which appear in the solar spectrum. This difference, however, is not taken account of in Vogel’s classification of stellar spectra. It may be added that photographs of the spectra of other stars resembling $\gamma$ Cygni have been obtained since the date of the paper referred to.

At a still further stage of condensation we get stars in which there are only a relatively small number of lines, and these are lines which appear in the nebula. This similarity became evident at an early stage of the discussion of the photographic spectrum of the Orion nebula, and a comparison with the spectrum of $\alpha$ Andromedae was given in the paper communicated to the Royal Society, in November, 1892.‡

The first suggestion of such a relation appears to have been made by Dr. Scheiner, of Potsdam,§ who pointed out that the strong line at $\lambda$ 4471, which had been observed in the Orion nebula by Dr. Copeland, was also seen in the Potsdam photographs of the spectrum of Rigel. This line is one of the brightest in the nebula photographs now under discussion, and is seen in the spectra of a large number of stars of the type of Rigel and Bellatrix.

The spectra of such stars in the region between K and $\lambda$ 472 are described in my paper referred to above; and in Table IV. they are compared with the spectrum of the Orion nebula. It will be seen that out of 31 lines in the nebula in the region compared, 20 are coincident with stellar lines.||

|| It may be added that $D_9$, which appears bright in the nebula, was observed by Mr. Fowler as a dark line in the spectrum of $\gamma$ and $\xi$ Orionis, on Dec. 12, 1893, and in Rigel on March 4, 1894. It does not, however, appear in the spectrum of Sirius or $\alpha$ Lyrae. $D_9$ has also been photographed as a dark line in the spectra of $\beta$ and $\epsilon$ Orionis, by Mr. Campbell at the Lick Observatory. 'Astr. and Ast. Phys.,' May, 1894 p. 395.
Table IV.—Comparison of Orion Nebula with Stars of Groups II. and III.

(Region K to λ 472 Ångström).

<table>
<thead>
<tr>
<th>Orion nebula</th>
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<th>Group IIIγ</th>
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<td>(Hα) 3968 (5)</td>
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<td>3968</td>
<td>3968 (6)</td>
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<td>3984</td>
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<td>4177 (4)</td>
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<td>4340 (6)</td>
<td>4340 (6)</td>
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<td>4340</td>
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<td>4414-5 (3)</td>
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</table>
In the accompanying map (fig. 4) an attempt is made to show the gradual change of the bright lines of the nebulae and bright-line stars into dark ones as condensation proceeds. Not all the lines seen in the various spectra, but only those which best illustrate the results of progressive condensation, are dealt with. In the spectrum of the Orion nebula and planetary nebulae, the lines shown in the map are those which afterwards appear as bright lines in the bright-line stars, or as dark lines in some of the more condensed bodies. The lines mapped as belonging to the bright-line stars are those which appear twice in Professor Pickering's lists, to which reference has been made, except in the case of the important line at \( \lambda 4471 \), which has been included because it appears in P Cygni as well as in one of Pickering's types of bright-line stars. The dark lines shown in the spectra of stars of Groups II., III\(\alpha\), III\(\beta\), III\(\gamma\), IV\(\alpha\), and IV\(\beta\), are only those which show remarkable coincidences either amongst themselves or with the bright lines at the foot of the map. The approximate intensities of the various lines in the map are represented by their thicknesses.

If we consider, first, the question of the hydrogen lines, it will be seen that they begin to thin out as bright lines in the bright-line stars, and make their appearance as thin dark lines in Group II. From Group II. to Group IV. they thicken pretty regularly; but other causes besides temperature may possibly affect their apparent thickness, as I have previously pointed out.†

In addition to the lines of hydrogen, other lines, including the H and K lines of

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* See 'Phil. Trans.,' vol. 184, 1893, p. 725.
† Ibid., p. 688.
calcium, and the lines at $\lambda$ 4388 and $\lambda$ 4471, appear as dark lines at an early stage in Group II.

Other lines, however, do not appear dark until a later stage; $\lambda$ 4025, $\lambda$ 4069, and $\lambda$ 4269, for example, do not make their appearance as dark lines until Group IIIy, and others, such as $\lambda$ 4205, do not appear until Group IV is reached.

Some of the dark lines, as $\lambda$ 4025 and $\lambda$ 4471, have their maximum intensity in Group IIIy, whilst others are much less regular in their intensities in passing through the different groups.

![Diagram showing the gradual change of bright to dark lines in condensing swarms of meteorites.](image)

In general, it may be taken that the absence of some of the lines from Group II, and the earlier stages of Group III, is due to the approximate equality of the radiating and absorbing areas of the vapours producing such lines.

With the aid of a series of photographs taken with special exposures, it is possible to extend the comparison of the stars of Groups III$\beta$, and IIIy, with the nebula into the ultra-violet region of the spectrum. These photographs have been reduced by Mr. Shackleton. The coincidences are shown in Table V. In this table Groups II,
and III. are omitted, for the reason that their spectra beyond K are only photographed with great difficulty.*

The wave-lengths of the lines of the nebula are copied from Table I., and are expressed on Cornu's scale; those of the lines in the ultra-violet spectra of stars of Group III. are based on wave-lengths of the ultra-violet lines of hydrogen on Rowland's scale, according to Professor Hale.†

The wave-lengths have been left in these different scales, because the differences are only minute, and, in general, in the ultra-violet region, less than the assumed accuracy of the wave-lengths as determined by the instruments at our disposal.

* 'Phil. Trans.,' A, vol. 184, 1893, p. 701.
† 'Astr. and Ast.-Phys.,' vol. 11, 1892, p. 618.
Table V.—Comparison of the Orion Nebula with Stars of Group III. in the Ultra-Violet Region.

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<tr>
<td>(Hα) 3752 (1)</td>
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<td>(Hγ) 3770 (1)</td>
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<tr>
<td>(Hθ) 3796 (2)</td>
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<td></td>
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<td>3933.6</td>
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</table>
|               | 3933.6      | 3933.6    | 3933.6
VI. General Conclusions.

(1) The spectrum of the nebula of Orion is a compound one consisting of hydrogen lines, low temperature metallic lines and flutings, and high temperature lines. The mean temperature, however, is relatively low.  

(2) The spectrum is different in different parts of the nebula.

(3) The spectrum bears a striking resemblance to that of the planetary nebulae and bright-line stars.

(4) The suggestion, therefore, that these are bodies which must be closely associated in any valid scheme of classification is strengthened.

(5) Many of the lines which appear bright in the spectrum of the nebula appear dark in the spectra of stars of Groups II. and III., and in the earlier stars of Group IV.; and a gradual change from bright to dark lines has been found.

(6) The view, therefore, that bright-line stars occupy an intermediate position between nebulae and stars of Group III. is greatly strengthened by these researches.

I have to express my great obligations to Mr. Fowler for the zeal and patience which he displayed in taking the photographs under somewhat unfavourable conditions. He is responsible for the determination of the wave-lengths of the lines and has assisted in the discussion.

Messrs. Baxandall and Shackleton, computers to the Solar Physics Committee, have assisted in the preparation of the tables and the map illustrating the changes of spectrum with increasing condensation.

III. Propagation of Magnetization of Iron as affected by the Electric Currents in the Iron.

By J. Hopkinson, F.R.S., and E. Wilson.*

Received May 17.—Read May 31, 1894.

PART I.

It is not unfamiliar to those who have worked on large dynamos with the ballistic galvanometer, that the indications of the galvanometer do not give the whole changes which occur in the induction. Let the deflections of the galvanometer connected to an exploring coil be observed when the main current in the magnetic coils is reversed. The first elongation will be much greater than the second in the other direction, and probably the third greater than the second—showing that a continued current exists in one direction for a time comparable with the time of oscillation of the galvanometer. These effects cannot be got rid of, though they can be diminished by passing the exciting current through a non-inductive resistance and increasing the electromotive force employed. This if carried far enough would be effective if the iron of the cores were divided so that no currents could exist in the iron; but the currents in the iron, if the core is solid, continue for a considerable time and maintain the magnetism of the interior of the core in the direction it had before reversal of current. It was one of our objects to investigate this more closely by ascertaining the changes occurring at different depths in a core in terms of the time after reversal has been made.

The experiments were carried out in the Siemens Laboratory, King’s College, London; and the electro-magnet used is shown in fig. 1. It consists in its first form, the results of which though instructive are not satisfactory, of two vertical wrought-iron cores, 18 inches long and 4 inches diameter, wound with 2595 and 2613 turns respectively of No. 16 B.W.G. cotton-covered copper wire—the resistance of the two coils in series being 16.3 ohms. The yoke is of wrought-iron 4 inches square in section and 2 feet long. The pole-pieces are of wrought-iron 4 inches square, and all surfaces in contact are truly planed. One of the pole-pieces is turned down at the end, which butts on the other pole-piece, for half an inch of its length to a diameter of 4 inches; and three circular grooves are cut in the abutting face having mean

* The experimental work of this paper was in part carried out by three of the Student Demonstrators of the Siemens Laboratory, King’s College, London, Messrs. Brazil, Atchison, and Greenham. We wish to express our thanks to them for their zealous co-operation.
Fig. 7.

Fig. 9.

Fig. 9a.

Fig. 9b.
diameters of 2.6, 5.16, and 7.75 centims. respectively, for the purpose of inserting copper coils the ends of which are brought out by means of the radial slot shown in fig. 2. When the pole-pieces are brought into contact as shown in fig. 1, we have thus three exploring coils within the mass and a fourth was wound on the circular portion outside. These exploring coils are numbered 1, 2, 3, 4 respectively, starting with the coil of least diameter.

Fig. 3 gives a diagram of the apparatus and connections, in which A is a reversing switch for the purpose of reversing a current given by ten storage cells through the magnet windings in series; B is a Thomson graded galvanometer for measuring current; and C is a non-inductive resistance of about 16 ohms placed across the magnet coils for the purpose of diminishing the violence of the change on reversal. The maximum current given by the battery was 1.2 amperes. A D'Arsonval galvanometer of Professor Ayrton's type, D, of 320 ohms resistance; a resistance box E; and a key F were placed in circuit with any one of the exploring coils 1, 2, 3, 4, for the purpose of observing the electromotive force of that circuit. The method of experiment was as follows:—The current round the magnet limbs was suddenly reversed and readings on the D'Arsonval galvanometer were taken on each coil at known epochs after the reversal. The results are shown in fig. 4, in which the ordinates are the electromotive forces in C.G.S. units and the abscissæ are in seconds.

The portion of these curves up to two seconds was obtained by means of a ballistic galvanometer having a periodic time of fifty seconds, the key of its circuit being broken at known epochs after reversal. From the induction curve so obtained the electromotive force was found by differentiation.

The curve A which is superposed on curve 4 of fig. 4 gives the current round the magnet in the magnetizing coils. It is worth noting, that, as would be expected, it agrees with the curve 4. The potential of the battery was 1.2 amperes × 16.3 ohms = 19.6 volts. Take the points two seconds after reversal, the electromotive force in one coil is 330,000; multiplying this by 5208, the number of coils on the magnet, we have in absolute units 1,718,640,000 as the electromotive force on the coil due to electromagnetic change, or, say, 17.2 volts. Subtracting this from 19.6 we have 2.4. The electromotive force observed is 1.25 × 16.3 = 2.02. The difference between these could be fully accounted for by an error of ¼ second in the time of either observation.

The general character of the results was quite unexpected by us. Take coil No. 2 for example, the spot of light, on reversing the current in the magnet winding, would at once spring off to a considerable deflection, the deflection would presently diminish, attaining a minimum after about 6 seconds; the deflection would then again increase and attain a maximum greater than the first after 8 seconds, it would then diminish and rapidly die away.

To attempt a thorough explanation of the peculiarities of these curves would mean
solving the differential equation connecting induction with time and radius in the iron with the true relation of induction and magnetizing force. But we may inversely from these curves attempt to obtain an approximation to the cyclic curve of induction of the iron.

Let \( l \) be the mean length of lines of force in the magnet. Let \( n \) be the number of convolutions on the magnet, and let \( e \) be the current in amperes in the magnetizing coils at time \( t \). Then at this epoch the force due to the magnetizing coils is \( 4\pi ne/10l \). Call this \( H_1 \).

Next consider only one centimetre length of the magnet in the part between the pole-pieces which is circular and has coils 1, 2, 3, wound within its mass, and coil 4 wound outside. The area of each of the electromotive force curves of the coils 1, 2, 3, 4, up to the ordinate corresponding to any time, is equal to the total change of the induction up to that time.

In fig. 2 let \( A_1, A_2, A_3, A_4 \) be the areas in sq. centims. of coil 1 and the ring-shaped areas included between the coils 1, 2, 3, 4 respectively. Then the induction at time \( t \), as given by the integral of curve 1, divided by \( A_1 \) is the average induction per sq. centim. for this epoch over this area. Also, the induction at time \( t \), as given by the integral of curve 2, minus the induction for the same time, as given by the integral of curve 1, divided by \( A_2 \), is the average induction per sq. centim. for this area. Similarly, average induction per sq. centim. for \( A_3, A_4 \) can be found for any epoch.

Consider area \( A_1 \). It is obvious that all currents induced within the mass considered external to this area, due to changes of induction, plus the current in the magnetizing coil per centim. linear, at any epoch, go to magnetize this area, and, further, the induced currents in the outside of the area \( A_1 \) itself go to magnetize the interior portion of this area. We know the electromotive forces at the radii 1, 2, 3, 4, and the lengths in centims. of circles corresponding to these radii. From a knowledge of the specific resistance of the iron we can find the resistance, in ohms, of rings of the iron corresponding to these radii, having a cross-sectional area of 1 sq. centim. Let these resistances be respectively \( r_1, r_2, r_3, r_4 \). At time \( t \), let \( e_1, e_2, e_3, e_4 \) be the electromotive forces in volts at the radii 1, 2, 3, 4, then \( \frac{e_1}{r_1}, \frac{e_2}{r_2}, \frac{e_3}{r_3}, \frac{e_4}{r_4} \) are at this epoch the amperes per sq. centim. at these radii. Let a curve be drawn for this epoch, having amperes per sq. centim. for ordinates and radii in centims. for abscissae. Then the area of this curve, from radius 1 to radius 4, gives approximately the amperes per centim. due to changes of induction, and (neglecting the currents within the area considered) the algebraic sum of this force (call it \( H_2 \)), with the force due to the magnetizing coils (\( H_1 \)) at the epoch chosen, gives the resultant magnetizing force acting upon area \( A_1 \). If \( H \) is this resultant force, we have \( H = H_1 + H_2 \). Next draw a curve showing the relation between the induction per sq. centim. (B) and the resultant force (H) for different epochs. This curve should be an approximation to the cyclic curve of induction of the iron.
MESSRS. J. HOPKINSON AND E. WILSON ON THE

Fig. 10.

Fig. 13.

Fig. 13a.

Fig. 14.

Fig. 15.

Fig. 16.
MESSRS. J. HOPKINSON AND E. WILSON ON THE

The attempt to obtain an approximation to the cyclic curve of induction from the curves in fig. 4 was a failure, that is to say, the resulting curve did not resemble a cyclic curve of magnetization. This is due to imperfections of fit of the two faces, in one of which the exploring coils are imbedded. That this imperfection of fit will tend to have a serious effect upon the distribution of induction over the whole area is obvious on consideration. Take the closed curve abed in fig. 5, where AB is the junction between the pole pieces. If the space between the faces was appreciable, the force along bc and ad in the iron could be neglected in comparison with the forces in the non-magnetic spaces ab, cd. The magnetizing force is sensibly $4\pi c$, where c is the current passing through the closed curve. This may be made as small as we please. Therefore, the force along ab is equal to the force along dc. In our case the space between the faces is very small, but has still a tendency towards an equalizing of the induction per unit area over the whole surface.

To test this the following experiment was tried. At a distance of $2\frac{1}{2}$ inches from the abutting surfaces of the pole pieces four holes were drilled in one of the pole pieces in a plane parallel with the abutting surfaces, as shown in fig. 6. By means of a hooked wire we were able to thread an insulated copper wire through these holes, so as to enclose only the square area A, which is bounded by the drilled holes and has an area of $61$ sq. inch. The wire is indicated by the dotted lines. Fig. 7 gives two curves taken by the D'Arsonval in the manner already described for a reversal of the same current in the copper coils of the magnets. No. 1 (fig. 7) is the curve obtained from No. 1 coil (fig. 2) near the air space. No. 2 (fig. 7) is the curve obtained from the square coil shown in fig. 6. The difference is very marked and shows at once the effect of the small non-magnetic space which accounts for the large initial change of induction previously observed on the coils 1, 2, 3 in fig. 4. Similar holes were drilled in the yoke of the magnet in a plane midway between the vertical cores, having the same area of $61$ sq. inch; and on trial exactly the same form of curve was produced as is shown in No. 2 of fig. 7. This method of drilling holes in the mass is open to the objection that the form of the area is square.

Whilst the above experiments were being made the portion of the magnet to take the place of the pole-pieces previously used was being constructed as follows:—In fig. 8 the portion of the magnetic circuit resting upon the vertical cores consists of a centre rod $A_1$ of very soft Whitworth steel surrounded by tubes $A_2, A_3$ of the same material. The diameter of $A_1$ is 1 inch. The outside diameter of $A_2$ is $2\frac{1}{2}$ inches; and $A_3$ is 4 inches outside diameter between the cores of the magnet, but is 4 inches square at each end where it rests upon the magnet limbs. At the centre of the rod $A_1$ (longitudinally) a circular groove is turned down 1 millim. deep and 5 millims. wide, and also a longitudinal groove 1 millim. deep and 1 millim. wide is cut as shown in the figure for the purpose of leading a double silk covered copper wire from terminal $T_1$ to 9 convolutions at the centre and along the rod to terminal $T_2$. A similar groove is cut in the outside of the tube $A_2$, and a copper wire is carried from
terminal $T_3$ to 9 convolutions round the centre of the tube again along the groove to terminal $T_5$. Nine convolutions were also wound round the outside tube $A_3$, the ends of which are connected to the terminals $T_6$, $T_9$ respectively.

The tubes and rod were made by Sir J. Whitworth and Co., of Manchester, and a considerable force was required to drive the pieces into their proper position. Our best thanks are due to Professor Kennedy and his assistants for the putting together of these pieces by means of a 50-ton hydraulic testing machine. We are aware that the surfaces are somewhat scored by the hydraulic pressure, and the magnetic qualities may be slightly different for layers of the soft steel near these surfaces, but they serve just as well for the purpose of our experiments.

Systematic experiments were then commenced. The magnetizing coils on the magnets were placed in parallel with one another, and a total current of 1·75 amperes (that is, 87 ampere in each coil), due to 5 storage cells, was reversed through the coils. The arrangement of apparatus is shown in fig. 3, except that the pole-pieces are replaced by the soft steel tubes shown in fig. 8, and the non-inductive resistance C is removed. We have now three exploring coils instead of four, and these are marked 1, 2, 3 respectively, starting with the coil of smallest diameter. For the purpose of obtaining the current curve, the D'Arsonval was placed across a non-inductive resistance of $\frac{1}{8}$ ohm in the circuit of the magnetizing coils. Fig. 9 gives a set of curves obtained with the 5 cells, and also another set obtained by a reversal of 1·8 amperes given by 54 cells—a non-inductive resistance being placed in the circuit to adjust the current.

The effect of reversing the same maximum current with two different potentials is very marked. Take coil No. 1. With 5 cells the maximum rate of change of induction occurs at 9 seconds after reversal, at which epoch the current in the copper coils is about 1 ampere, the maximum current being 1·75. With 54 cells the maximum rate of change of induction occurs at 4 seconds, and here the current in the copper coils is nearly a maximum. We therefore chose to work with 54 cells, thus avoiding a magnetizing force due to the current in the copper coils varying for considerable times after reversal.
Fig. 17.

Fig. 18.

Fig. 19.
PROPAGATION OF MAGNETIZATION OF IRON.

Fig. 19a.

Fig. 19a—continued.

Fig. 19b.

Fig. 19c.

Fig. 19d.
Table I. gives a list of the experiments made with total reversal of current due to 54 cells, the magnetizing coils being kept in parallel with one another, and the magnitude of current through them adjusted by means of a non-inductive resistance.

In fig. 10 the maximum current in the copper coils is 0·0745 ampere, which, after reversal, passes through zero and attains a maximum at about 3 seconds. It will be observed that the change of induction with regard to each of the coils 1, 2, 3 is rapid to begin with, but that it gradually decays and becomes zero at about 46 seconds after reversal.

Fig. 11 is interesting in that it gives the particular force at which coils 1 and 2 show a second rise in the electromotive force curves, No. 1 being a maximum at about 25 seconds, and No. 2 at about 8 seconds after reversal. These "humps" become a flat on the curve for a little smaller force, and, as shown in fig. 10, they have disappeared altogether. In this case the current in the copper coils has attained a maximum at about 4 seconds after reversal.

In fig. 12 the maximum current in the copper coils is 2·24 ampere, corresponding with a force in C.G.S. units of 4·96. This is got from \( \frac{4\pi}{10} \times \frac{2600 \times 0.24}{158} \). The current in the copper coils has attained its maximum value at about 4 seconds after reversal, and changes of induction were going on up to 35 seconds.

In the following attempt to obtain an approximation to the cyclic curve of hysteresis, from these curves, we have taken the volume-specific resistance of the soft steel to be \( 13 \times 10^{-6} \) ohm. We have taken the diameter of coils 1, 2, 3 to be respectively 1·22, 3·18, and 5·08 centims.; and we find that the corresponding resistances, in ohms, of rings of the steel having 1 sq. centim. cross-section and mean diameters equal to the coils are, respectively, \( 103·7 \times 10^{-6} \), \( 259·4 \times 10^{-6} \), and \( 416·4 \times 10^{-6} \). From a knowledge of the electromotive forces at the three radii, for a given epoch, we are able to find the amperes per sq. centim. at those radii. In fig. 12A a series of curves have been drawn for different epochs, giving the relation between amperes per sq. centim. and radii in centims., and the areas of these curves between different limits have been found, and are tabulated in Table II. It is necessary here to state that the path of these curves through the four given points in each case is assumed; we have simply drawn a fair curve through the points. But what we wish to show is that the results obtained with the curves, drawn as shown in fig. 12A, are not inconsistent with what we know with great probability to be true.

The results shown in fig. 12B have been obtained as follows: take curve I, fig. 12B; the electromotive force curve of coil 1, fig. 12, has been integrated, and the integral up to the ordinate corresponding to any time is equal to the total.

* In Part II. of this paper the smallest radius was taken to be 1·27. For our purpose the difference is not worth the expense of correction.
change of the induction up to that time, which divided by the area of the coil in sq. centims. gives the average induction per sq. centim. In obtaining the areas we had to assume the path of the electromotive force curve up to 2 seconds, but this we can do with a good deal of certainty.

With regard to the forces we see that after 3 seconds the induced currents have to work against a constant current in the copper coils. In obtaining the forces due to induced currents we have only taken the area of the curves in fig. 12A between the radii 1.22 centims. and 5.08 centims.; that is, we have neglected the effect of the currents within the area of coil No. 1 altogether. The resultant force (H) is the algebraic sum of the force (H2) due to the currents between the radii taken, and the force (H3) due to the current in the copper coils, and is set forth for different epochs in Table II. The inductions per sq. centim. have been plotted in terms of this resultant force (H), and curve I., fig. 12B, shows this relation.

Next, take curves II. and III., fig. 12B. In obtaining the inductions for these curves, the difference between the integrals of curves No. 1 and 2, fig. 12, for a given epoch, has been taken. This gives the induction for this epoch, which, when divided by the ring-shaped area between coils 1 and 2, gives the average induction per unit of that area.

In obtaining the forces in curve II., fig. 12B, we have taken the areas of the curves in fig. 12A between the radii 3.18 centims. and 5.08 centims.; that is, we have neglected the forces within the area under consideration as before. Here the error is of more importance, and may partly account for the difference between the forces of curves I., II. In curve III. we have taken the areas of curves in fig. 12A between the radii 2.2 and 5.08; that is, we have taken account of the force due to induced currents over a considerable portion of the area considered. Coupled with the uncertainty in form of the curves in fig. 12A we have the uncertainty as to how much to allow for the forces due to induced currents over the particular area considered. The difference in the ordinates of curves I. and II. may partly be accounted for by errors arising from the assumed path of the electromotive force curve up to 2 seconds, which is more uncertain in curve 2, fig. 12, than in curve 1; and partly to possible slight inequality between the materials of the rod and its surrounding tube.

In fig. 13 the maximum current in the copper coils is .77 ampere, corresponding with a force in C.G.S. units of 16. The current in the copper coils, after passing through zero, attains its full value at about 9 seconds after reversal, and the change of induction ceases at 10 seconds.

No. 1 curve, fig. 13, has been integrated, and the maximum induction per sq. centim. found to be 14,500 C.G.S. units. We have taken a given cyclic curve for soft iron corresponding with this maximum induction, and have tabulated the forces obtained therefrom in Table III. for the different values of B got from the integration of No. 1 curve. We then plotted in fig. 13A the amperes per sq. centim.

MDCCXCV.—A. P
Fig. 20.

Fig. 20a.

Fig. 20b.

Fig. 20c.
Fig. 21.

Fig. 21a.

Fig. 21c.

Fig. 21d.
at the different radii for different epochs, and in each case, by drawing a curve fairly through them, we were able to produce areas in fair correspondence with areas as got by means of the given cyclic curve. The comparative areas are tabulated in Table III.

In fig. 9 the maximum current in the copper coils due to the 54 cells is 1·8 amperes, corresponding with a force of 20·7 in C.G.S. units. In this case the current had passed through zero and attained a maximum at 6 seconds after reversal; the change of induction being zero also at this time. We have worked out the current per sq. centim. for the different radii at different epochs, as before, and have plotted them in fig. 9A. Fig 9B gives the relation of \( B \) to \( H \), found from the curves, and it also shows a fair approximation to the cyclic curve for soft iron, although in this case the points are fewer in number and were more difficult to obtain, owing to the greater rapidity with which the D'Arsonval needle moved as compared with the earlier curves.

With a reversal of 2·3 amperes the whole induction effects had died out at 5 seconds after reversal. Coil No. 1 showed a maximum electromotive force at about 3\( \frac{1}{2} \) seconds. Coil No. 2 gave a dwell, and attained a maximum at 2 seconds, and then died rapidly away. Coil No. 3 attained an immediate maximum and died rapidly to zero at 5 seconds.

With a reversal of 6\( \frac{1}{2} \) amperes the whole inductive effects had died out at about 3 seconds after reversal. No. 1 coil showed a maximum electromotive force at about 1\( \frac{3}{4} \) seconds. No. 2 gave a dwell and attained a maximum at about 1\( \frac{1}{2} \) seconds and rapidly died away to zero at about 2 seconds. No. 3 attained an immediate maximum and died rapidly to zero at about 2 seconds.

The variations in form of these curves and of the times the electromotive forces take to die away are intimately connected with the curve of magnetization of the material. When the magnetizing force is small (1·7) the maxima occur early because the ratio induction to magnetizing force is small. As the magnetizing force increases to 3 and 4·96 the maxima occur later because this ratio has increased, whilst when the force is further increased to 16 and 37·2, as shown in figs. 13 and 9, the maxima occur earlier because the ratio has again diminished.

The results, both of these experiments and of those which follow, have a more general application than to bars of the particular size used. From the dimensions of the partial differential equation which expresses the propagation of induction in the bar, one sees at once that if the external magnetizing forces are the same in two bars differing in diameter, then similar magnetic events will occur in the two bars, but at times varying as the square of the diameters of the bars. But one may see this equally without referring to the differential equation. Suppose two bars, one \( n \) times the diameter of the other, in which there are equal variations of the magnetizing forces; consider the annulus between radii \( r_1, r_2 \) and \( nr_1, nr_2 \) in the two, the resistance per centimetre length of the rods of these annuli will be the same for
their area, and their lengths are alike as 1 : \( n \); the inductions through them, when the inductions per centimetre are the same, are as the areas, that is, as 1 : \( n^2 \). Hence if the inductions change at rates inversely proportional to 1 : \( n^2 \), the currents between corresponding radii will be the same at times in the ratio of 1 : \( n^2 \), and the magnetizing forces will also be the same.

Magnets of sixteen inches diameter are not uncommon; with such a magnet, the magnetizing force being 37 and the magnetizing current being compelled to at once attain its full value, it will take over a minute for the centre of the iron to attain its full inductive value.

On the other hand, with a wire or bundle of wires, each 1 millim. diameter, and a magnetizing force between 3 and 5, which gives the longest times with our bar, the centre of the wire will be experiencing its greatest rate of change in about \( \frac{1}{30} \) second. This is a magnetizing force similar to those used in transformers, and naturally leads us to the second part of our experiments.

**Part II.—Alternate Currents.**

This part of the subject has a practical bearing in the case of alternate current transformer cores, and the armature cores of dynamo-electric machines.

The alternate currents used have periodic times, varying from 4 to 80 seconds, and were obtained from a battery of 54 storage cells by means of a liquid reverser,* shown in elevation and plan in figs. 14 and 15. It consists of two upright curved plates of sheet copper, AA, between which were rotated two similar plates, BB, connected with collecting rings, DD, from which the current was led away by brushes to the primary circuit of the magnet. The copper plates are placed in a weak solution of copper sulphate in a porcelain jar. The inner copper plates, and the collecting rings, are fixed to a vertical shaft, S, which can be rotated at any desired speed by means of the gearing shown in the figure. The outer plates are connected to the terminals of the battery of storage cells, and the arrangement gives approximately a sine curve of current when working through a non-inductive resistance.

The experiments were made with the same electro-magnet and Whitworth steel tubes described in Part I. of this paper. Fig. 16 gives a diagram of connections in which M is the current reverser, G is the Thomson graded current meter for measuring the maximum current in the copper coils, and W is the electro-magnet. A small, non-inductive resistance, placed in the primary circuit served to give the curve of current by observations on the D'Arsonval galvanometer, D, of the time variation of the potential difference between its ends. The D'Arsonval galvanometer was also used, as in Part I., for observing the electromotive forces of the exploring coils 1, 2, and 3 (see fig. 8, Part I.), R being an adjustable resistance in its circuit for the purpose of keeping the deflections on the scale.

* This form of reverser is due to Professor Ewing.
Fig. 22.

![Graph showing the relationship between current, time, and amperes in copper coils.](image)

Fig. 22a.

![Graph showing the relationship between amperes per cm and radii in cm.](image)

Fig. 22b.

![Graph illustrating another set of data points.](image)
The method of experiment was as follows:—The liquid reverser, M, was placed so as to give a maximum current on the meter G, which was adjusted by non-inductive resistance, N, to the desired value, and, in all cases, when changing from higher to lower currents, a system of demagnetization by reversals was adopted. Time was taken, as in Part I., on a clock beating seconds, which could be heard distinctly.

As an example, take fig. 19, in which the periodic time is 80 seconds, and the maximum current in the copper coils 23 ampere. The E.M.F. curves of the exploring coils are numbered 1, 2, and 3 respectively, and the curve of current in the copper coils is also given.

As in the case of simple reversals (Part I.) we may from these curves attempt to obtain an approximation to the cyclic curve of induction of the iron. In all cases where this is done we have taken coil 1 and considered the area within it—that is to say, from a knowledge of the E.M.F.'s at different depths of the iron, due to change of induction at any epoch, we have estimated the average magnetizing force acting in this area, and this we call $H_3$. The curves from which these forces have been obtained are given in fig. 19A, and have been plotted from Table VI. The algebraic sum of this force, $H_3$, and the force $H_1$, given at the same epoch by the current in the copper coils, is taken to be the \emph{then} resultant force magnetizing this area. Also the integral of curve 1, fig. 19, gives the average induction over this area at the same epoch. Curve $x$, fig. 19B, is the cyclic curve obtained by plotting the inductions in terms of the resultant force $H$.

A word is necessary with regard to the last column in Table VI. This gives the total dissipation of energy by induced currents in ergs per cycle per cub. centim. of the iron. We know the watts per sq. centim. at different depths of the iron for different epochs. Let a series of curves be drawn (fig. 19c) for chosen epochs giving this relation: the areas of these curves from radii 0 to 5.08 give for the respective epochs the watts per centim. dissipated by induced currents. In symbols this is

\[ \int_{\text{sq. centim.}} \frac{ec}{dr} \text{ dr} \]

where $r$ is the radius, and $ec$ the E.M.F. and current. It is now only necessary to integrate with regard to time in order to obtain the total dissipation: we have chosen a half period as our limits. This gives us

\[ \int_{\text{sq. centim.}} \frac{ec}{dr} \text{ dr} \text{ dt} \]

and is got from the area of curve $z$, fig. 19d. The ordinates of this curve are taken from the last column of Table VI.

The curves in figs. 21, 22, have been treated in a similar manner to that already described in connection with fig. 19. But in fig. 20 the procedure is a little different. In this case the periodic time is 20, and the maximum force per centim. linear, due to the current in the copper coils, is 4.87. With this frequency and current the effects of induced currents in the iron are very marked: we have taken a given soft iron cyclic curve, of roughly the same maximum induction as given by the integral of curve No. 1, fig. 20, and have tabulated the forces obtained therefrom in Table VII.
In fig. 20a we have plotted the amperes per sq. centim. at the different radii, and for the several epochs, and in each case, by drawing a curve fairly through these points, as shown in the figure, we are able to produce areas in fair correspondence with the areas obtained by means of the given cyclic curve. The comparative areas are given in Table VII.

The results shown in fig. 22 are by no means so satisfactory as the results given by other figures, but we have thought it better to insert them here, as we do not wish to make any selection of results which might give an idea of average accuracy greater than these experiments are entitled to.

Referring now to the summary of results in Table V., we note the marked effect of change of frequency upon the average induction per unit area of the innermost coil No. 1, when dealing with comparatively small maximum inductions. Compare the results given in figs. 19 and 20. The maximum force per centim. linear due to the current in the copper coils is 4'8 in each case, but the average induction per sq. centim. of coil No. 1 is reduced from 7690 to 1630 by a change of frequency from $\frac{1}{80}$ to $\frac{1}{20}$. This is, of course, not the case on the higher portion of the induction curve, as is shown by the results of figs. 21 and 22, although the resultant force $H$ is reduced by the induced currents.

In fig. 23 the maximum amperes in the copper coils is '24, and the periodic time is reduced to 4. An inspection of these curves shows the marked effect of change of frequency, coil No. 2 being exceedingly diminished in amplitude as compared with No. 3.

As an example of the practical bearing of this portion of the paper, suppose we have a transformer core made out of iron wire, 1 millim. in diameter, the wires being perfectly insulated from one another. The outside diameter of our outer tube is 101'6 millims. Similar events will therefore happen at times, varying as $\left(\frac{1}{101'6}\right)^2$.

Take the case of fig. 19, in which the periodic time is 80 seconds, and the maximum average induction per sq. centim. is about 7000.

$$\frac{(101'6)^2}{80} = 129$$ periods per second, and this is an example which might arise in practice. The ergs dissipated per cycle per cu.b. centim. are 3820 by induced currents, and about 3000 by magnetic hysteresis. We see further, from fig. 20, that at 500 periods per second only the outside layers of our 1 millim. wire are really useful.

As another example, take the case of an armature core of a dynamo electric machine in which a frequency of 1000 complete periods per minute might be taken.

In fig. 21 the periodic time is 80, and the maximum average induction per sq. centim. is 15,000.

We have

$$1 = 80 \left(\frac{x}{101'6}\right)^2$$

$$x = 101'6/36 = \text{nearly 3 millims.}$$

MDCCXCV. — A.
The ergs dissipated per cycle per cub. centim. are 26,000 by induced currents, and about 17,000 by magnetic hysteresis. This shows that according to good practice, where the wires in armature cores are of an order of 1 or 2 millims. diameter, the loss by induced currents would be but small as compared with the loss by magnetic hysteresis. This, of course, assumes the wires to be perfectly insulated from one another, which is not always realised in practice.

Both the armature cores of dynamos and the cores of transformers are now usually made of plates instead of wire; roughly speaking a plate in regard to induced currents in its substance is comparable to a wire of a diameter double the thickness of the plate. We infer that the ordinary practice of making transformer plates about $\frac{1}{2}$ millim. thick, and plates of armature cores 1 millim. thick, is not far wrong. Not much is lost by local currents in the iron, and the plates could not be much thicker without loss.*

Table I.

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* The question of dissipation of energy by local currents in iron has been discussed by Professors J. J. Thomson and Ewing. See the 'Electrician,' April 8th and 15th, 1892.
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**TABLE II.**

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<th>Curve II and III.</th>
<th>Radius in cm.</th>
<th>( H )</th>
<th>Amperage per cm.</th>
<th>( E ) in Volts in 10-c.</th>
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**PROPA GATION OF MAGNETIZATION OF IRON.**
Table III.

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<th>Time in seconds after reversal</th>
<th>Area in ( \frac{1}{4} ) diagram squares Figs. 13 and 15</th>
<th>Charge of inductive current per sq. cm. in Coils.</th>
<th>Induction per sq. cm.</th>
<th>Radius 1.22 cm.</th>
<th>Radius 3.18 cm.</th>
<th>Radius 5.08 cm.</th>
<th>Force due to current in magnets H.</th>
<th>Force taken from the given cyclic curve, H.</th>
<th>Difference of forces, H. and H.</th>
<th>Area in 4 diagram squares corresponding to differences of forces, H. and H.</th>
<th>Area in 4 diagram squares of curves in Fig. 13A</th>
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### Table IV

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<th>Induction, Hr. cm.</th>
<th>Radius 122 cm.</th>
<th>Radius 128 cm.</th>
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<td>E.M.F. in volts in $10^{-6}$.</td>
<td>Amperes per sq. cm.</td>
<td>E.M.F. in volts in $10^{-6}$.</td>
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### Table V

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<th>No. 3.</th>
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**Proposition of Magnetization of Iron**
**Table VI.**—Periodic Time, 80 seconds. Maximum Current in Copper Coils, 23 amperes.

<table>
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<tr>
<th>Time in seconds</th>
<th>Coil 1</th>
<th>Coil 2</th>
<th>Coil 3</th>
<th>Average induction per sq. cm. of Coil 1</th>
<th>Current in copper coils</th>
<th>Inductive force due to induced currents</th>
<th>Reactive magnetic force per cm.</th>
<th>Energy dissipated by induced currents</th>
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<td>Amperage per sq. cm.</td>
<td>EMF in 160 volts per turn.</td>
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**Notes:**
- EMF: Electromotive Force
- Amperage: Current in amperes
- Periodic Time: 80 seconds
- Maximum Current: 23 amperes
**Propagation of Magnetization of Iron.**

<table>
<thead>
<tr>
<th>Current in Copper Coils</th>
<th>110</th>
<th>0.06</th>
<th>0.04</th>
<th>0.02</th>
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<tr>
<td>Wave in Core in 100 &amp;</td>
<td>0.6</td>
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<td>from Induction on Core.</td>
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<td>0.2</td>
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**Table VII—Periodic Time, 20 seconds. Maximum Current in Copper Coils, 23 amperes.**

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<td>0.2</td>
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<td>mm. of Copper Coils.</td>
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<td>0.4</td>
<td>0.2</td>
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**Note:**

- Induction per mm. of copper coils.
- Wave per cm. in 100 & from induction on core.
### Table VIII—Periodic Time, 80 seconds. Maximum Current in Copper Coils, 1.06 amperes.

<table>
<thead>
<tr>
<th>Column</th>
<th>Current in Copper Coils</th>
<th>Average Induction at Central Point</th>
<th>Deduction of Amperage</th>
<th>Induction at One End of Coil 1</th>
<th>Induction at One End of Coil 2</th>
<th>Average for 80 seconds</th>
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Table IX.—Periodic Time, 20 seconds. Maximum Current in Copper Coils, 1.06 amperes.

<table>
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<tr>
<th>Time in seconds</th>
<th>E.M.F. in 10^-4 volts per turn.</th>
<th>Amperes per sq. cm.</th>
<th>Watts per sq. cm. in E.M.F.</th>
<th>Amperes per sq. cm. in deflection on Amperemeter, E.M.F. in 10^-4 volts per turn.</th>
<th>Watts per sq. cm.</th>
<th>Area of E.M.F. in sq. cm. in other arm.</th>
<th>Average, induction per sq. cm. of Coll 1.</th>
<th>Current in copper coils.</th>
<th>Magnetostriction force due to induced currents.</th>
<th>Force per cm. Hanau.</th>
<th>Resultant magnetising force per cm.</th>
<th>Energy dissipated by induced currents.</th>
<th>Watts per cm. in 10^-4</th>
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By Osborne Reynolds, M.A., LL.D., F.R.S., Professor of Engineering in Owens College, Manchester.

Received April 25—Read May 24, 1894.

Section I.

Introduction.

1. The equations of motion of viscous fluid (obtained by grafting on certain terms to the abstract equations of the Eulerian form so as to adapt these equations to the case of fluids subject to stresses depending in some hypothetical manner on the rates of distortion, which equations Navier* seems to have first introduced in 1822, and which were much studied by Cauchy† and Poisson‡) were finally shown by St. Venant§ and Sir Gabriel Stokes|| in 1845, to involve no other assumption than that the stresses, other than that of pressure uniform in all directions, are linear functions of the rates of distortion, with a co-efficient depending on the physical state of the fluid.

By obtaining a singular solution of these equations as applied to the case of pendulums in steady periodic motion, Sir G. Stokes¶ was able to compare the theoretical results with the numerous experiments that had been recorded, with the result that the theoretical calculations agreed so closely with the experimental determinations as seemingly to prove the truth of the assumption involved. This was also the result of comparing the flow of water through uniform tubes with the flow calculated from a singular solution of the equations so long as the tubes were small and the velocities slow. On the other hand, these results, both theoretical and practical, were directly at variance with common experience as to the resistance

* 'Mém. de l'Académie,' vol. 6, p. 389.
† 'Mém. des Savants Étrangers,' vol. 1, p. 40.
‡ 'Mém. de l'Académie,' vol. 10, p. 345.
§ 'B.A. Report,' 1846.
|| 'Cambridge Phil. Trans.,' 1845.
¶ 'Cambridge Phil. Trans.,' vol. 9, 1857.
encountered by larger bodies moving with higher velocities through water, or by water moving with greater velocities through larger tubes. This discrepancy Sir G. Stokes considered as probably resulting from eddies which rendered the actual motion other than that to which the singular solution referred and not as disproving the assumption.

In 1850, after Joule's discovery of the Mechanical Equivalent of Heat, Stokes showed, by transforming the equations of motion—with arbitrary stresses—so as to obtain the equations of ("Vis-viva") energy, that this equation contained a definite function, which represented the difference between the work done on the fluid by the stresses and the rate of increase of the energy, per unit of volume, which function, he concluded, must, according to Joule, represent the Vis-viva converted into heat.

This conclusion was obtained from the equations irrespective of any particular relation between the stresses and the rates of distortion. Sir G. Stokes, however, translated the function into an expression in terms of the rates of distortion, which expression has since been named by Lord Rayleigh the Dissipation-Function.

2. In 1883 I succeeded in proving, by means of experiments with colour bands—the results of which were communicated to the Society*—that when water is caused by pressure to flow through a uniform smooth pipe, the motion of the water is direct, i.e., parallel to the sides of the pipe, or sinuous, i.e., crossing and re-crossing the pipe, according as $U_m$, the mean velocity of the water, as measured by dividing $Q$, the discharge, by $\Delta$, the area of the section of the pipe, is below or above a certain value given by

$$K \mu / D \rho,$$

where $D$ is the diameter of the pipe, $\rho$ the density of the water, and $K$ a numerical constant, the value of which according to my experiments and, as I was able to show, to all the experiments by Poiseuille and Darcy, is for pipes of circular section between

1900 and 2000,

or, in other words, steady direct motion in round tubes is stable or unstable according as

$$\rho \frac{D U_m}{\mu} < 1900 \text{ or } > 2000,$$

the number $K$ being thus a criterion of the possible maintenance of sinuous or eddying motion.

3. The experiments also showed that $K$ was equally a criterion of the law of the resistance to be overcome—which changes from a resistance proportional to the

* 'Phil. Trans.' 1883. Part III., p. 935.
velocity and in exact accordance with the theoretical results obtained from the singular solution of the equation, when direct motion changes to sinuous, i.e., when

\[ \rho \frac{DU_m}{\mu} = K. \]

4. In the same paper I pointed out that the existence of this sudden change in the law of motion of fluids between solid surfaces when

\[ DU_m = \mu \frac{\rho}{K} \]

proved the dependence of the manner of motion of the fluid on a relation between the product of the dimensions of the pipe multiplied by the velocity of the fluid and the product of the molecular dimensions multiplied by the molecular velocities which determine the value of \( \mu \) for the fluid, also that the equations of motion for viscous fluid contained evidence of this relation.

These experimental results completely removed the discrepancy previously noticed, showing that, whatever may be the cause, in those cases in which the experimental results do not accord with those obtained by the singular solution of the equations, the actual motions of the water are different. But in this there is only a partial explanation, for there remains the mechanical or physical significance of the existence of the criterion to be explained.

5. [My object in this paper is to show that the theoretical existence of an inferior limit to the criterion follows from the equations of motion as a consequence:—

(1) Of a more rigorous examination and definition of the geometrical basis on which the analytical method of distinguishing between molar-motions and heat-motions in the kinetic theory of matter is founded; and

(2) Of the application of the same method of analysis, thus definitely founded, to distinguish between mean-molar-motions and relative-molar-motions where, as in the case of steady-mean-flow along a pipe, the more rigorous definition of the geometrical basis shows the method to be strictly applicable, and in other cases where it is approximately applicable.

The geometrical relation of the motions respectively indicated by the terms mean-molar-, or Mean-Mean-Motion, and relative-molar or Relative-Mean-Motion being essentially the same as the relation of the respective motions indicated by the terms molar-, or Mean-Motion, and relative-, or Heat-Motion, as used in the theory of gases.

I also show that the limit to the criterion obtained by this method of analysis and by integrating the equations of motion in space, appears as a geometrical limit to the
possible simultaneous distribution of certain quantities in space, and in no wise depends on the physical significance of these quantities. Yet the physical significance of these quantities, as defined in the equations, becomes so clearly exposed as to indicate that further study of the equations would elucidate the properties of matter and mechanical principles involved, and so be the means of explaining what has hitherto been obscure in the connection between thermodynamics and the principles of mechanics.

The geometrical basis of the method of analysis used in the kinetic theory of gases has hitherto consisted:—

(1) Of the geometrical principle that the motion of any point of a mechanical system may, at any instant, be abstracted into the mean motion of the whole system at that instant, and the motion of the point relative to the mean-motion; and

(2) Of the assumption that the component, in any particular direction, of the velocity of a molecule may be abstracted into a mean-component-velocity (say \( u \)) which is the mean-component velocity of all the molecules in the immediate neighbourhood, and a relative velocity (say \( \xi \)), which is the difference between \( u \) and the component-velocity of the molecule;* \( u \) and \( \xi \) being so related that, \( M \) being the mass of the molecule, the integrals of \( (M\xi) \) and \( (Mu\xi) \), &c., over all the molecules in the immediate neighbourhood are zero, and \( \Sigma [(M(u + \xi)^2) = \Sigma [M(u^2 + \xi^2)]. \)

The geometrical principle (1) has only been used to distinguish between the energy of the mean-motion of the molecule and the energy of its internal motions taken relatively to its mean motion; and so to eliminate the internal motions from all further geometrical considerations which rest on the assumption (2).

That this assumption (2) is purely geometrical, becomes at once obvious, when it is noticed that the argument relates solely to the distribution in space of certain quantities at a particular instant of time. And it appears that the questions as to whether the assumed distinctions are possible under any distributions, and, if so, under what distribution, are proper subjects for geometrical solution.

On putting aside the apparent obviousness of the assumption (2), and considering definitely what it implies, the necessity for further definition at once appears.

The mean component-velocity (\( u \)) of all the molecules in the immediate neighbourhood of a point, say \( P \), can only be the mean component-velocity of all the molecules in some space (S) enclosing \( P \). \( u \) is then the mean-component velocity of the mechanical system enclosed in \( S \), and, for this system, is the mean velocity at every point within \( S \), and multiplied by the entire mass within \( S \) is the whole component momentum of the system. But, according to the assumption (2), \( u \) with its derivatives are to be continuous functions of the position of \( P \), which functions may vary from point to point even within \( S \); so that \( u \) is not taken to represent the mean component-velocity of the system within \( S \), but the mean-velocity at the point \( P \). Although there seems to have been no specific statement to that effect, it is presumable that the space \( S \) has

* "Dynamical Theory of Gases," 'Phil. Trans.,' 1866, pp. 67. † 'Phil. Trans.,' 1866, p. 71.
been assumed to be so taken that $P$ is the centre of gravity of the system within $S$. The relative positions of $P$ and $S$ being so defined, the shape and size of the space $S$ requires to be further defined, so that $u$, &c., may vary continuously with the position of $P$, which is a condition that can always be satisfied if the size and shape of $S$ may vary continuously with the position of $P$.

Having thus defined the relation of $P$ to $S$ and the shape and size of the latter, expressions may be obtained for the conditions of distribution of $u$, for which $\Sigma (M\xi)$ taken over $S$ will be zero, i.e., for which the condition of mean-momentum shall be satisfied.

Takings $S_1$, $u_1$, &c., as relating to a point $P_1$ and $S$, $u$, &c., as relating to $P$, another point of which the component distances from $P_1$ are $x$, $y$, $z$, $P_1$ is the C.G. of $S_1$, and by however much or little $S$ may overlap $S_1$, $S$ has its centre of gravity at $x$, $y$, $z$, and is so chosen that $u$, &c., may be continuous functions of $x$, $y$, $z$. $u$ may, therefore, differ from $u_1$ even if $P$ is within $S_1$. Let $u$ be taken for every molecule of the system $S$. Then according to assumption (2), $\Sigma (Mx)$ over $S_1$ must represent the component of momentum of the system within $S_1$, that is, in order to satisfy the condition of mean momentum, the mean-value of the variable quantity $u$ over the system $S_1$ must be equal to $u_1$ the mean-component velocity of the system $S_1$, and this is a condition which in consequence the geometrical definition already mentioned can only be satisfied under certain distributions of $u$. For since $u$ is a continuous function of $x$, $y$, $z$, $M (u - u_1)$ may be expressed as a function of the derivatives of $u$ at $P_1$ multiplied by corresponding powers and products of $x$, $y$, $z$, and again by $M$; and by equating the integral of this function over the space $S_1$ to zero, a definite expression is obtained, in terms of the limits imposed on $x$, $y$, $z$, by the already defined space $S_1$ for the geometrical condition as to the distribution of $u$ under which the condition of mean momentum can be satisfied.

From this definite expression it appears, as has been obvious all through the argument, that the condition is satisfied if $u$ is constant. It also appears that there are certain other well-defined systems of distribution for which the condition is strictly satisfied, and that for all other distributions of $u$ the condition of mean-momentum can only be approximately satisfied to a degree for which definite expressions appear.

Having obtained the expression for the condition of distribution of $u$, so as to satisfy the condition of mean momentum, by means of the expression for $M (u - u')$, &c., expressions are obtained for the conditions as to the distribution of $\xi$, &c., in order that the integrals over the space $S_1$ of the products $M (u\xi)$, &c., may be zero when $\Sigma [M (u - u_1)] = 0$, and the conditions of mean energy satisfied as well as those of mean-momentum. It then appears that in some particular cases of distribution of $u$, under which the condition of mean momentum is strictly satisfied, certain conditions as to the distribution of $\xi$, &c., must be satisfied in order that the energies of mean-
and relative-motion may be distinct. These conditions as to the distribution of $\xi, \&c.$, are, however, obviously satisfied in the case of heat motion, and do not present themselves otherwise in this paper.

From the definite geometrical basis thus obtained, and the definite expressions which follow for the condition of distribution of $u, \&c.$, under which the method of analysis is strictly applicable, it appears that this method may be rendered generally applicable to any system of motion by a slight adaptation of the meaning of the symbols, and that it does not necessitate the elimination of the internal motion of the molecules, as has been the custom in the theory of gases.

Taking $u, v, w$ to represent the motions (continuous or discontinuous) of the matter passing a point, and $\rho$ to represent the density at the point, and putting $\bar{u}, \&c.$, for the mean-motion (instead of $u$ as above), and $u', \&c.$, for the relative-motion (instead of $\xi$ as before), the geometrical conditions as to the distribution of $\bar{u}, \&c.$, to satisfy the conditions of mean-momentum and mean-energy are, substituting $\rho$ for $M$, of precisely the same form as before, and as thus expressed, the theorem is applicable to any mechanical system however abstract.

(1) In order to obtain the conditions of distribution of molar-motion, under which the condition of mean-momentum will be satisfied so that the energy of molar-motion may be separated from that of the heat-motion, $u, \&c.$, and $\rho$ are taken as referring to the actual motion and density at a point in a molecule, and $S_1$ is taken of such dimensions as may correspond to the scale, or periods in space, of the molecular distances, then the conditions of distribution of $\bar{u}$, under which the condition of mean-momentum is satisfied, become the conditions as to the distribution of molar-motion, under which it is possible to distinguish between the energies of molar-motions and heat-motions.

(2) And, when the conditions in (1) are satisfied to a sufficient degree of approximation by taking $u$ to represent the molar-motion ($\bar{u}$ in (1)), and the dimensions of the space $S$ to correspond with the period in space or scale of any possible periodic or eddying motion. The conditions as to the distribution of $\bar{u}, \&c.$ (the components of mean-mean-motion), which satisfy the condition of mean-momentum, show the conditions of mean-molar-motion, under which it is possible to separate the energy of mean-molar-motion from the energy of relative-molar- (or relative-mean-) motion.

Having thus placed the analytical method used in the kinetic theory on a definite geometrical basis, and adapted so as to render it applicable to all systems of motion, by applying it to the dynamical theory of viscous fluid, I have been able to show:—Feb. 18, 1895.]

(a) That the adoption of the conclusion arrived at by Sir Gabriel Stokes, that the dissipation function represents the rate at which heat is produced, adds a definition to the meaning of $u, v, w$—the components of mean or fluid velocity—which was previously wanting:
FLUIDS AND THE DETERMINATION OF THE CRITERION.

(b) That as the result of this definition the equations are true, and are only true as applied to fluid in which the mean-motions of the matter, excluding the heat-motions, are steady;

(c) That the evidence of the possible existence of such steady mean-motions, while at the same time the conversion of the energy of these mean-motions into heat is going on, proves the existence of some discriminative cause by which the periods in space and time of the mean-motion are prevented from approximating in magnitude to the corresponding periods of the heat-motions, and also proves the existence of some general action by which the energy of mean-motion is continually transformed into the energy of heat-motion without passing through any intermediate stage;

(d) That as applied to fluid in unsteady mean-motion (excluding the heat-motions), however steady the mean integral flow may be, the equations are approximately true in a degree which increases with the ratios of the magnitudes of the periods, in time and space, of the mean-motion to the magnitude of the corresponding periods of the heat-motions;

(e) That if the discriminative cause and the action of transformation are the result of general properties of matter, and not of properties which affect only the ultimate motions, there must exist evidence of similar actions as between the mean-mean-motion, in directions of mean flow, and the periodic mean-motions taken relative to the mean-mean-motion but excluding heat-motions. And that such evidence must be of a general and important kind, such as the unexplained laws of the resistance of fluid motions, the law of the universal dissipation of energy and the second law of thermodynamics;

(f) That the generality of the effects of the properties on which the action of transformation depends is proved by the fact that resistance, other than proportional to the velocity, is caused by the relative (eddying) mean-motion.

(g) That the existence of the discriminative cause is directly proved by the existence of the criterion, the dependence of which on circumstances which limit the magnitudes of the periods of relative mean-motion, as compared with the heat-motion, also proves the generality of the effects of the properties on which it depends.

(h) That the proof of the generality of the effects of the properties on which the discriminative cause, and the action of transformation depend, shows that—if in the equations of motion the mean-mean-motion is distinguished from the relative-mean-motion in the same way as the mean-motion is distinguished from the heat-motions—(1) the equations must contain expressions for the transformation of the energy of mean-mean-motion to energy of relative-mean-motion; and (2) that the equations, when integrated over a complete system, must show that the possibility of relative-mean-motion depends on the ratio of the possible magnitudes of the periods of relative-mean-motion, as compared with the corresponding magnitude of the periods of the heat-motions.

(i) That when the equations are transformed so as to distinguish between the MDCCCXCIV.—A.
mean-mean-motions, of infinite periods, and the relative-mean-motions of finite periods, there result two distinct systems of equations, one system for mean-mean-motion, as affected by relative-mean-motion and heat-motion, the other system for relative-mean-motion as affected by mean-mean-motion and heat-motions.

(j) That the equation of energy of mean-mean-motion, as obtained from the first system, shows that the rate of increase of energy is diminished by conversion into heat, and by transformation of energy of mean-mean-motion in consequence of the relative-mean-motion, which transformation is expressed by a function identical in form with that which expresses the conversion into heat; and that the equation of energy of relative-mean-motion, obtained from the second system, shows that this energy is increased only by transformation of energy from mean-mean-motion expressed by the same function, and diminished only by the conversion of energy of relative-mean-motion into heat.

(k) That the difference of the two rates (1) transformation of energy of mean-mean-motion into energy of relative-mean-motion as expressed by the transformation function, (2) the conversion of energy of relative-mean-motion into heat, as expressed by the function expressing dissipation of the energy of relative-mean-motion, affords a discriminating equation as to the conditions under which relative-mean-motion can be maintained.

(l) That this discriminating equation is independent of the energy of relative-mean-motion, and expresses a relation between variations of mean-mean-motion of the first order, the space periods of relative-mean-motion and \( \mu/\rho \) such that any circumstances which determine the maximum periods of the relative-mean-motion determine the conditions of mean-mean-motion under which relative mean-motion will be maintained —determine the criterion.

(m) That as applied to water in steady mean flow between parallel plane surfaces, the boundary conditions and the equation of continuity impose limits to the maximum space periods of relative-mean-motion such that the discriminating equation affords definite proof that when an indefinitely small sinuous or relative disturbance exists it must fade away if

\[ \rho DU_m/\mu \]

is less than a certain number, which depends on the shape of the section of the boundaries, and is constant as long as there is geometrical similarity. While for greater values of this function, in so far as the discriminating equation shows, the energy of sinuous motion may increase until it reaches to a definite limit, and rules the resistance.

(n) That besides thus affording a mechanical explanation of the existence of the criterion K, the discriminating equation shows the purely geometrical circumstances on which the value of K depends, and although these circumstances must satisfy geometrical conditions required for steady mean-motion other than those imposed by
the conservations of mean energy and momentum, the theory admits of the determination of an inferior limit to the value of $K$ under any definite boundary conditions, which, as determined for the particular case, is

517.

This is below the experimental value for round pipes, and is about half what might be expected to be the experimental value for a flat pipe, which leaves a margin to meet the other kinematical conditions for steady mean-mean-motion.

(o) That the discriminating equation also affords a definite expression for the resistance, which proves that, with smooth fixed boundaries, the conditions of dynamical similarity under any geometrical similar circumstances depend only on the value of

$$\frac{\rho}{\mu^3} \frac{dp}{dx} b^3,$$

where $b$ is one of the lateral dimensions of the pipe; and that the expression for this resistance is complex, but shows that above the critical velocity the relative-mean-motion is limited, and that the resistances increase as a power of the velocity higher than the first.

**Section II.**

The Mean-motion and Heat-motions as distinguished by Periods.—Mean-mean-motion and Relative-mean-motion.— Discriminative Cause and Action of Transformation.—Two Systems of Equations.—A Discriminating Equation.

6. Taking the general equations of motion for incompressible fluid, subject to no external forces to be expressed by

\[
\begin{align*}
\rho \frac{dw}{dt} &= - \left\{ \frac{d}{dx} (\rho_{xx} + \rho_{uu}) + \frac{d}{dy} (\rho_{xy} + \rho_{uv}) + \frac{d}{dz} (\rho_{xz} + \rho_{uw}) \right\}, \\
\rho \frac{dv}{dt} &= - \left\{ \frac{d}{dx} (\rho_{yx} + \rho_{vu}) + \frac{d}{dy} (\rho_{yy} + \rho_{vv}) + \frac{d}{dz} (\rho_{yz} + \rho_{vw}) \right\}, \\
\rho \frac{dw}{dt} &= - \left\{ \frac{d}{dx} (\rho_{zx} + \rho_{wu}) + \frac{d}{dy} (\rho_{zy} + \rho_{wv}) + \frac{d}{dz} (\rho_{zz} + \rho_{ww}) \right\}
\end{align*}
\]

with the equation of continuity

\[
0 = dw/dx + dv/dy + dw/dz . . . . . . . . . . (2),
\]

where $\rho_{xx}$, &c., are arbitrary expressions for the component forces per unit of area, resulting from the stresses, acting on the negative faces of planes perpendicular to
the direction indicated by the first suffix, in the direction indicated by the second suffix.

Then multiplying these equations respectively by \( u, v, w \), integrating by parts, adding and putting

\[
2E \text{ for } \rho (u^2 + v^2 + w^2)
\]

and transposing, the rate of increase of kinetic energy per unit of volume is given by

\[
\left( \frac{d}{dt} + u \frac{d}{dx} + v \frac{d}{dy} + w \frac{d}{dz} \right) E = - \left\{ \frac{d}{dx} (wp_{zx}) + \frac{d}{dy} (wp_{zy}) + \frac{d}{dz} (wp_{zz}) \right\} 
+ \left\{ p_{xx} \frac{du}{dx} + p_{yx} \frac{du}{dy} + p_{xz} \frac{du}{dz} \right\} 
+ \left\{ p_{xy} \frac{dv}{dx} + p_{yy} \frac{dv}{dy} + p_{yz} \frac{dv}{dz} \right\} 
+ \left\{ p_{xz} \frac{dw}{dx} + p_{yz} \frac{dw}{dy} + p_{zz} \frac{dw}{dz} \right\}
\]

The left member of this equation expresses the rate of increase in the kinetic energy of the fluid per unit of volume at a point moving with the fluid.

The first term on the right expresses the rate at which work is being done by the surrounding fluid per unit of volume at a point.

The second term on the right therefore, by the law of conservation of energy, expresses the difference between the rate of increase of kinetic energy and the rate at which work is being done by the stresses. This difference has, so far as I am aware, in the absence of other forces, or any changes of potential energy, been equated to the rate at which heat is being converted into energy of motion, Sir Gabriel Stokes having first indicated this* as resulting from the law of conservation of energy then just established by Joule.

7. This conclusion, that the second term on the right of (3) expresses the rate at which heat is being converted, as it is usually accepted, may be correct enough, but there is a consequence of adopting this conclusion which enters largely into the method of reasoning in this paper, but which, so far as I know, has not previously received any definite notice.

* 'Cambridge Phil. Trans.,' vol. 9, p. 57.
The Component Velocities in the Equations of Viscous Fluids.

In no case, that I am aware of, has any very strict definition of \( u, v, w \), as they occur in the equations of motion, been attempted. They are usually defined as the velocities of a particle at a point \((x, y, z)\) of the fluid, which may mean that they are the actual component velocities of the point in the matter passing at the instant, or that they are the mean velocities of all the matter in some space enclosing the point, or which passes the point in an interval of time. If the first view is taken, then the right hand member of the equation represents the rate of increase of kinetic energy, per unit of volume, in the matter at the point; and the integral of this expression over any finite space \( S \), moving with the fluid, represents the total rate of increase of kinetic energy, including heat-motion, within that space; hence the difference between the rate at which work is done on the surface of \( S \), and the rate at which kinetic energy is increasing can, by the law of conservation of energy, only represent the rate at which that part of the heat which does not consist in kinetic energy of matter is being produced, whence it follows:—

(a) That the adoption of the conclusion that the second term in equation (3) expresses the rate at which heat is being converted, defines \( u, v, w \), as not representing the component velocities of points in the passing matter.

Further, if it is understood that \( u, v, w \), represent the mean velocities of the matter in some space, enclosing \( x, y, z \), the point considered, or the mean velocities at a point taken over a certain interval of time, so that \( \Sigma (\rho u), \Sigma (\rho v), \Sigma (\rho w) \) may express the components of momentum, and \( z\Sigma (\rho v) - y\Sigma (\rho w), \&c., \&c., \) may express the components of moments of momentum, of the matter over which the mean is taken; there still remains the question as to what spaces and what intervals of time?

(b) Hence the conclusion that the second term expresses the rate of conversion of heat, defines the spaces and intervals of time over which the mean component velocities must be taken, so that \( E \) may include all the energy of mean-motion, and exclude that of heat-motions.

Equations Approximate only except in Three Particular Cases.

8. According to the reasoning of the last article, if the second term on the right of equation (3) expresses the rate at which heat is being converted into energy of mean-motion, either \( \rho u, \rho v, \rho w \) express the mean components of momentum of the matter, taken at any instant over a space \( S_0 \) enclosing the point \( x, y, z \), to which \( u, v, w \) refer, so that this point is the centre of gravity of the matter within \( S_0 \) and such that \( \rho \) represents the mean density of the matter within this space; or \( \rho u, \rho v, \rho w \) represent the mean components of momentum taken at \( x, y, z \) over an interval of time \( \tau \), such that \( \rho \) is the mean density over the time \( \tau \), and if \( t \) marks the instant to which \( u, v, w \) refer, and \( t' \) any other instant, \( \Sigma [(t - t') \rho] \), in which \( \rho \) is the actual density, taken over the interval \( \tau \) is zero. The equations, however, require, that so obtained,
\[ \rho, u, v, w, \] shall be continuous functions of space and time, and it can be shown that this involves certain conditions between the distribution of the mean-motion and the dimensions of \( S_0 \) and \( r \).

\[ \text{Mean- and Relative-Motions of Matter.} \]

Whatever the motions of matter within a fixed space \( S \) may be at any instant, if the component velocities at a point are expressed by \( u, v, w \), the mean component velocities taken over \( S \) will be expressed by

\[
\bar{u} = \frac{\Sigma (\rho u)}{\Sigma \rho}, \quad \&c., \quad \&c. \quad \ldots \ldots \ldots \ldots \ldots \quad (4).
\]

If then \( \bar{u}, \bar{v}, \bar{w} \), are taken at each instant as the velocities of \( x, y, z \), the instantaneous centre of gravity of the matter within \( S \), the component momentum at the centre of gravity may be put

\[
\rho \mathbf{u} = \rho \bar{\mathbf{u}} + \rho \mathbf{u}' \quad \ldots \ldots \ldots \ldots \ldots \quad (5),
\]

where \( \mathbf{u}' \) is the motion of the matter, relative to axes moving with the mean velocity, at the centre of gravity of the matter within \( S \). Since a space \( S \) of definite size and shape may be taken about any point \( x, y, z \) in an indefinitely larger space, so that \( x, y, z \) is the centre of gravity of the matter within \( S \), the motion in the larger space may be divided into two distinct systems of motion, of which \( \bar{u}, \bar{v}, \bar{w} \) represent a mean-motion at each point and \( u', v', w' \) a motion at the same point relative to the mean-motion at the point.

If, however, \( \bar{u}, \bar{v}, \bar{w} \) are to represent the real mean-motion, it is necessary that \( \Sigma (\rho u'), \Sigma (\rho v'), \Sigma (\rho w') \) summed over the space \( S \), taken about any point, shall be severally zero; and in order that this may be so, certain conditions must be fulfilled.

For taking \( x, y, z \) for \( G \) the centre of gravity of the matter within \( S \) and \( x', y', z' \) for any other point within \( S \), and putting \( a, b, c \) for the dimensions of \( S \) in directions \( x, y, z \), measured from the point \( x, y, z \), since \( \bar{u}, \bar{v}, \bar{w} \) are continuous functions of \( x, y, z \), by shifting \( S \) so that the centre of gravity of the matter within it is at \( x', y', z' \), the value of \( \bar{u} \) for this point is given by

\[
\bar{u} = \bar{u}_g + (x' - x) \left( \frac{du}{dx} \right)_g + (y' - y) \left( \frac{du}{dy} \right)_g + (z' - z) \left( \frac{du}{dz} \right)_g + \frac{1}{2} (x' - x)^2 \left( \frac{d^2 u}{d\phi'^2} \right)_g + \&c. \quad (6)
\]

where all the differential coefficients on the left refer to the point \( x, y, z \); and in the same way for \( \bar{v} \) and \( \bar{w} \).

Subtracting the value of \( \bar{u} \) thus obtained for the point \( x', y', z' \) from that of \( u \) at the
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same point the difference is the value of \( u' \) at this point, whence summing these differences over the space \( S \) about \( G \) at \( x, y, z \), since by definition when summed over the space \( S \) about \( G \)

\[
\Sigma [\rho (u - \bar{u}_G)] = 0 \quad \text{and} \quad \Sigma [\rho (x - x)] = 0 \quad \ldots \quad (7)
\]

\[
\Sigma (\rho u') = - \left\{ \frac{1}{2} \Sigma [\rho (x - x')^2] \left( \frac{d^2 u}{dx^2} \right)_g + \frac{1}{2} \Sigma [\rho (y - y')^2] \left( \frac{d^2 u}{dy^2} \right)_g + \frac{1}{2} \Sigma [\rho (z - z')^2] \left( \frac{d^2 u}{dz^2} \right)_g + \&c. \right\}
\]

That is

\[
\frac{\Sigma (\rho u')}{\Sigma (\rho)} \text{ is } < \left\{ \frac{a^2}{2} \left( \frac{d^2 u}{dx^2} \right)_g + \frac{b^2}{2} \left( \frac{d^2 u}{dy^2} \right)_g + c^2 \left( \frac{d^2 u}{dz^2} \right)_g + \&c. \right\}
\]

In the same way if \( \Sigma (\quad ) \) be taken over the interval of time \( \tau \) including \( t \); and for the instant \( \tau \)

\[
\bar{u} = \frac{\Sigma (\rho u)}{\Sigma (\rho)}, \quad \text{and} \quad \rho \bar{u} = \rho u + \rho u';
\]

then since for any other instant \( t' \)

\[
\bar{u} = \bar{u}_t + (t - t') \left( \frac{d\bar{u}}{dt} \right)_t + \frac{1}{2} (t - t')^2 \left( \frac{d^2 \bar{u}}{dt^2} \right)_t + \&c.,
\]

where \( \Sigma [\rho (t - t')] = 0 \), and \( \Sigma [\rho (\bar{u}_t - u)] = 0 \).

It appears that

\[
\Sigma (\rho u') = - \Sigma \left[ \frac{1}{2} \rho (t - t')^2 \right] \frac{d^2 \bar{u}}{dt^2} + \&c.
\]

\[
\frac{\Sigma (\rho u')}{\Sigma (\rho)} \text{ is } < - \frac{1}{2} \tau^2 \left( \frac{d^2 \bar{u}}{dt^2} \right)_t + \&c.
\]

From equations (8A) and (8B), and similar equations for \( \Sigma (\rho v') \) and \( \Sigma (\rho w') \), it appears that if

\[
\Sigma (\rho u') = \Sigma (\rho v') = \Sigma (\rho w') = 0,
\]

where the summation extends both over the space \( S \) and the interval \( \tau \), all the terms on the right of equations (8A) and (8B) must be respectively and continuously zero, or, what is the same thing, all the differential coefficients of \( \bar{u}, \bar{v}, \bar{w} \) with respect to \( x, y, z \) and \( t \) of the first order must be respectively constant.

This condition will be satisfied if the mean-motion is steady, or uniformly varying
with the time, and is everywhere in the same direction, being subject to no variations in the direction of motion; for suppose the direction of motion to be that of \( \mathbf{a} \), then since the periodic motion passes through a complete period within the distance \( 2a \), \( \Sigma (\rho u') \) will be zero within the space
\[
2a \, dy \, dz,
\]
however small \( dy \, dz \) may be, and since the only variations of the mean-motion are in directions \( y \) and \( z \), in which \( b \) and \( c \) may be taken zero, and \( du/dt \) is everywhere constant, the conditions are perfectly satisfied.

The conditions are also satisfied if the mean-motion is that of uniform expansion or contraction, or that of a rigid body.

These three cases, in which it may be noticed that variations of mean-motion are everywhere uniform in the direction of motion, and subject to steady variations in respect of time, are the only cases in which the conditions (8A), (8B), can be perfectly satisfied.

The conditions will, however, be approximately satisfied, when the variations of \( \bar{u}, \bar{v}, \bar{w} \) of the first order are approximately constant over the space \( S \).

In such case the right-hand members of equations (8A), (8B), are neglected, and it appears that the closeness of the approximations will be measured by the relative magnitude of such terms as
\[
\alpha \, d^2u/dx^2, \, \&c., \tau \, d^2u/dt^2 \text{ as compared with } du/dx, d\bar{u}/dt, \&c.
\]

Since frequent reference must be made to these relative values, and, as in periodic motion, the relative values of such terms are measured by the period (in space or time) as compared with \( \alpha, b, c \) and \( \tau \), which are, in a sense, the periods of \( u', v', w' \), I shall use the term period in this sense, taking note of the fact that when the mean-motion is constant in the direction of motion, or varies uniformly in respect of time, it is not periodic, i.e., its periods are infinite.

9. It is thus seen that the closeness of the approximation with which the motion of any system can be expressed as a varying mean-motion together with a relative-motion, which, when integrated over a space of which the dimensions are \( \alpha, b, c \), has no momentum, increases as the magnitude of the periods of \( u, v, w \) in comparison with the periods of \( u', v', w' \), and is measured by the ratio of the relative orders of magnitudes to which these periods belong.

**Heat-motions in Matter are Approximately Relative to the Mean-motions.**

The general experience that heat in no way affects the momentum of matter, shows that the heat-motions are relative to the mean-motions of matter taken over spaces of
sensible size. But, as heat is by no means the only state of relative-motion of matter, if the heat-motions are relative to all mean-motions of matter, whatsoever their periods may be, it follows—that there must be some discriminative cause which prevents the existence of relative-motions of matter other than heat, except mean-motions with periods in time and space of greatly higher orders of magnitude than the corresponding periods of the heat-motions—otherwise, by equations (8A), (8B), heat-motions could not be to a high degree of approximation relative to all other motions, and we could not have to a high degree of approximation,

\[
P_{xx} \frac{du}{dx} + P_{xy} \frac{du}{dy} + P_{xz} \frac{du}{dz}
\]

\[
P_{xy} \frac{dv}{dx} + P_{yy} \frac{dv}{dy} + P_{yz} \frac{dv}{dz}
\]

\[
P_{xz} \frac{dw}{dx} + P_{yz} \frac{dw}{dy} + P_{zz} \frac{dw}{dz}
\]

\[= - \frac{d}{dt} (P_H) \] ... (9),

where the expression on the right stands for the rate at which heat is converted into energy of mean-motion.


10. The recognition of the existence of a discriminative cause, which prevents the existence of relative-mean-motions with periods of the same order of magnitude as heat-motions, proves the existence of another general action by which the energy of relative-mean-motion, of which the periods are of another and higher order of magnitude than those of the heat-motions, is transformed to energy of heat-motion.

For if relative-mean-motions cannot exist with periods approximating to those of heat, the conversion of energy of mean-motion into energy of heat, proved by Joule, cannot proceed by the gradual degradation of the periods of mean-motion until these periods coincide with those of heat, but must, in its final stages, at all events, be the result of some action which causes the energy of relative-mean-motion to be transformed into the energy of heat-motions without intermediate existence in states of relative-motion with intermediate and gradually diminishing periods.

That such change of energy of mean-motion to energy of heat may be properly called transformation becomes apparent when it is remembered that neither mean-motion nor relative-motion have any separate existence, but are only abstract quantities, determined by the particular process of abstraction, and so changes in the actual-motion may, by the process of abstraction, cause transformation of the abstract energy of the one abstract-motion, to abstract energy of the other abstract-motion.

All such transformation must depend on the changes in the actual-motions, and so...
must depend on mechanical principles and the properties of matter, and hence the
direct passage of energy of relative-mean-motion to energy of heat-motions is evidence
of a general cause of the condition of actual-motion which results in transformation—
which may be called the cause of transformation.

The Discriminative Cause, and the Cause of Transformation.

11. The only known characteristic of heat-motions, besides that of being relative
to the mean-motion, already mentioned, is that the motions of matter which result
from heat are an ultimate form of motion which does not alter so long as the mean-
motion is uniform over the space, and so long as no change of state occurs in the
matter. In respect of this characteristic, heat-motions are, so far as we know,
unique, and it would appear that heat-motions are distinguished from the mean-
motions by some ultimate properties of matter.

It does not, however, follow that the cause of transformation, or even the
discriminative cause, are determined by these properties. Whether this is so or not
can only be ascertained by experience. If either or both these causes depend solely
on properties of matter which only affect the heat-motions, then no similar effect
would result as between the variations of mean-mean-motion and relative-mean-
motion, whatever might be the difference in magnitude of their respective periods.
Whereas, if these causes depend on properties of matter which affect all modes of
motion, distinctions in periods must exist between mean-mean-motion and relative-
mean-motion, and transformation of energy take place from one to the other, as
between the mean-motion and the heat-motions.

The mean-mean-motion cannot, however, under any circumstances stand to the
relative-mean-motion in the same relation as the mean-motion stands to the heat-
motions, because the heat-motions cannot be absent, and in addition to any trans-
formation from mean-mean-motion to relative-mean-motion, there are transformations
both from mean- and relative-mean-motion to heat-motions, which transformation
may have important effects on both the transformation of energy from mean-
to relative-mean-motion, and on the discriminative cause of distinction in their periods.

In spite of the confusing effect of the ever present heat-motions, it would, however,
seem that evidence as to the character of the properties on which the cause of trans-
formation and the discriminative cause depend should be forthcoming as the result of
observing the mean- and relative-mean-motions of matter.

12. To prove by experimental evidence that the effects of these properties of
matter are confined to the heat-motions, would be to prove a negative; but if these
properties are in any degree common to all modes of matter, then at first sight it
must seem in the highest degree improbable that the effects of these causes on the
mean- and relative-mean-motions would be obscure, and only to be observed by
delicate tests. For properties which can cause distinctions between the mean- and
heat-motions of matter so fundamental and general, that from the time these motions were first recognized the distinction has been accepted as part of the order of nature, and has been so familiar to us that its cause has excited no curiosity, cannot, if they have any effect at all, but cause effects which are general and important on the mean-motions of matter. It would thus seem that evidence of the general effects of such properties should be sought in those laws and phenomena known to us as the result of experience, but of which no rational explanation has hitherto been found; such as the law that the resistance of fluids moving between solid surfaces and of solids moving through fluids, in such a manner that the general-motion is not periodic, is as the square of the velocities, the evidence covered by the law of the universal tendency of all energy to dissipation and the second law of thermodynamics.

13. In considering the first of the instances mentioned, it will be seen that the evidence it affords as to the general effect of the properties, on which depends transformation of energy from mean- to relative-motion, is very direct. For, since my experiments with colour bands have shown that when the resistance of fluids, in steady mean flow, varies with a power of the velocity higher than the first the fluid is always in a state of sinuous motion, it appears that the prevalence of such resistance is evidence of the existence of a general action by which energy of mean-mean-motion with infinite periods is directly transformed to the energy of relative-mean-motion, with finite periods, represented by the eddying motion, which renders the general mean-motion sinuous, by which transformation the state of eddying-motion is maintained, notwithstanding the continual transformation of its energy into heat-motions.

We have thus direct evidence that properties of matter which determine the cause of transformation, produce general and important effects which are not confined to the heat-motions.

In the same way, the experimental demonstration I was able to obtain, that relative-mean-motion in the form of eddies of finite periods, both as shown by colour bands and as shown by the law of resistances, cannot be maintained except under circumstances depending on the conditions which determine the superior limits to the velocity of the mean-mean-motion, of infinite periods, and the periods of the relative-mean-motion, as defined in the criterion

\[ \frac{DU_{st}}{\mu} = K, \]

is not only a direct experimental proof of the existence of a discriminative cause which prevents the maintenance of periodic mean-motion except with periods greatly in excess of the periods of the heat-motions, but also indicates that the discriminative cause depends on properties of matter which affect the mean-motions as well as the heat-motions.
Expressions for the Rate of Transformation and the Discriminative Cause.

14. It has already been shown (Art. 8) that the equations of motion approximate to a true expression of the relations between the mean-motions and stresses, when the ratio of the periods of mean-motions to the periods of the heat-motions approximates to infinity. Hence it follows that these equations must of necessity include whatever mechanical or kinematical principles are involved in the transformation of energy of mean-mean-motion to energy of relative-mean-motion. It has also been shown that the properties of matter on which depends the transformation of energy of varying mean-motion to relative-motion are common to the relative-mean-motion as well as to the heat-motion. Hence, if the equations of motion are applied to a condition in which the mean-motion consists of two components, the one component being a mean-mean-motion, as obtained by integrating the mean-motion over spaces $S$, taken about the point $x, y, z$, as centre of gravity, and the other component being a relative-mean-motion, of which the mean components of momentum taken over the space $S$ everywhere vanish, it follows:

1. That the resulting equations of motion must contain an expression for the rate of transformation from energy of mean-mean-motion to energy of relative-mean-motion, as well as the expressions for the transformation of the respective energies of mean- and relative-mean-motion to energy of heat-motion;

2. That, when integrated over a complete system these equations must show that the possibility of the maintenance of the energy of relative-mean-motion depends, whatsoever may be the conditions, on the possible order of magnitudes of the periods of the relative-mean-motion, as compared with the periods of the heat-motions.

The Equations of Mean- and Relative Mean-Motion.

15. These last conclusions, besides bringing the general results of the previous argument to the test point, suggest the manner of adaptation of the equations of motion, by which the test may be applied.

Put

\[ u = \overline{u} + v', \quad v = \overline{v} + v', \quad w = \overline{w} + w'. \quad \ldots \quad (11), \]

where

\[ \overline{u} = \Sigma (\rho u) / \Sigma (\rho), \text{ &c., &c.} \quad \ldots \quad (12), \]

the summation extending over the space $S$, of which the centre of gravity is at the
point \(x, y, z\). Then since \(u, v, w\) are continuous functions of \(x, y, z\), therefore \(\bar{u}, \bar{v}, \bar{w}\), and \(u', v', w'\), are continuous functions of \(x, y, z\). And as \(\rho\) is assumed constant, the equations of continuity for the two systems of motion are:

\[
\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} = 0 \quad \text{and} \quad \frac{du'}{dx} + \frac{dv'}{dy} + \frac{dw'}{dz} = 0 \quad \ldots \quad (13);
\]

also both systems of motions must satisfy the boundary conditions, whatever they may be.

Further putting \(\bar{p}_{xx}, \&c.,\) for the mean values of the stresses taken over the space \(S_1\) and

\[
p'_{xx} = p_{xx} - \bar{p}_{xx} \quad \ldots \quad (14)
\]

and defining \(S_1\) to be such that the space variations of \(\bar{u}, \bar{v}, \bar{w}\) are approximately constant over this space, we have, putting \(\bar{u}u', \&c.,\) for the mean values of the squares and products of the components of relative-mean-motion, for the equations of mean-mean-motion,

\[
\rho \frac{du}{dt} = -\left\{ \frac{d}{dx} (\bar{p}_{xx} + \bar{p}^{uu} + \bar{p}^{uv}u') + \frac{d}{dy} (\bar{p}_{yx} + \bar{p}^{uv} + \bar{p}^{vw}v') + \frac{d}{dz} (\bar{p}_{zx} + \bar{p}^{uw} + \bar{p}^{wu}w') \right\} \quad \ldots \quad (15),
\]

\&c. = \&c.
\&c. = \&c.

which equations are approximately true at every point in the same sense as that in which the equations (1) of mean-motion are true.

Subtracting these equations of mean-mean-motion from the equations of mean-motion, we have

\[
\rho \frac{dv'}{dt} = -\left\{ \frac{d}{dx} \left[ p'_{xx} + \rho \left( \bar{u}w' + u'\bar{w} \right) + \rho \left( u'u' - \bar{u}^2 \right) \right] \\
+ \frac{d}{dy} \left[ p'_{yx} + \rho \left( \bar{w}v' + u'\bar{v} \right) + \rho \left( u'v' - \bar{u}v \right) \right] \\
+ \frac{d}{dz} \left[ p'_{zx} + \rho \left( \bar{w}w' + u'\bar{w} \right) + \rho \left( u'w' - \bar{u}w \right) \right] \right\} \&c., \&c. \quad (16),
\]

which are the equations of momentum of relative-mean-motion at each point.
Again, multiplying the equations of mean-mean-motion by $\overline{u}$, $\overline{v}$, $\overline{w}$ respectively, adding and putting $2E = \rho (\overline{u}^2 + \overline{v}^2 + \overline{w}^2)$, we obtain

$$
\left( \frac{d}{dt} + u \frac{d}{dx} + v \frac{d}{dy} + w \frac{d}{dz} \right) E =
$$

$$
- \left\{ \frac{d}{dx} \left[ \overline{u} (\overline{p}_{xx} + u' u') \right] + \frac{d}{dy} \left[ \overline{v} (\overline{p}_{yy} + v' v') \right] + \frac{d}{dz} \left[ \overline{w} (\overline{p}_{zz} + w' w') \right] \right\}
$$

$$
+ \left\{ \frac{d}{dx} \left[ \overline{u} \overline{p}_{xx} \right] + \frac{d}{dy} \left[ \overline{v} \overline{p}_{yy} \right] + \frac{d}{dz} \left[ \overline{w} \overline{p}_{zz} \right] \right\}
$$

$$
+ \left\{ \frac{d}{dx} \left[ \overline{u} \overline{w} \frac{du}{dx} + \overline{v} \overline{w} \frac{dv}{dy} + \overline{w} \overline{w} \frac{dw}{dz} \right] \right\}
$$

which is the approximate equation of energy of mean-mean-motion in the same sense as the equation (3) of energy of mean-motion is approximate.

In a similar manner multiplying the equations (16) for the momentum of relative-mean-motion respectively by $u'$, $v'$, $w'$, and adding, the result would be the equation for energy of relative-mean-motion at a point, but this would include terms of which the mean values taken over the space $S_1$ are zero, and, since all corresponding terms in the energy of heat are excluded, by summation over the space $S_0$ in the expression for the rate at which mean-motion is transformed into heat, there is no reason to include them for the space $S_1$; so that, omitting all such terms and putting

$$
2E' = \rho (\overline{u}^2 + \overline{v}^2 + \overline{w}^2) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (18),
$$

we obtain
\[
\left( \frac{d}{dt} + u \frac{d}{dx} + v \frac{d}{dy} + w \frac{d}{dz} \right) E' =
\]
\[
+ \frac{d}{dx} \left[ u' (p'_{xx} + \rho w' u') \right] + \frac{d}{dy} \left[ v' (p'_{yy} + v' u') \right] + \frac{d}{dz} \left[ w' (p'_{zz} + w' u') \right]
\]
\[
- \left\{ \begin{array}{l}
\frac{d}{dx} \left[ u' (p'_{xx} + v' u') \right] + \frac{d}{dy} \left[ v' (p'_{yy} + v' u') \right] + \frac{d}{dz} \left[ w' (p'_{zz} + v' u') \right] \\
\frac{d}{dx} \left[ v' (p'_{zy} + v' u') \right] + \frac{d}{dy} \left[ w' (p'_{zy} + v' u') \right] + \frac{d}{dz} \left[ u' (p'_{zy} + w' u') \right]
\end{array} \right. \]
\[
+ \begin{pmatrix}
p'_{zz} \frac{d}{dx} \frac{d u}{d x} + p'_{zy} \frac{d}{dx} \frac{d w}{d x} + p'_{zz} \frac{d}{dx} \frac{d w}{d x} \\
p'_{zy} \frac{d}{dx} \frac{d v}{d x} + p'_{zz} \frac{d}{dx} \frac{d v}{d x} + p'_{zy} \frac{d}{dx} \frac{d v}{d x} \\
p'_{xz} \frac{d}{dx} \frac{d w}{d x} + p'_{yz} \frac{d}{dx} \frac{d v}{d x} + p'_{xz} \frac{d}{dx} \frac{d v}{d x}
\end{pmatrix}
\]
\[
- \begin{pmatrix}
\rho u' \frac{d}{dx} \frac{d u}{d x} + \rho v' \frac{d}{dx} \frac{d w}{d x} + \rho w' \frac{d}{dx} \frac{d w}{d x} \\
\rho v' \frac{d}{dx} \frac{d v}{d x} + \rho w' \frac{d}{dx} \frac{d v}{d x} + \rho w' \frac{d}{dx} \frac{d v}{d x} \\
\rho w' \frac{d}{dx} \frac{d w}{d x} + \rho v' \frac{d}{dx} \frac{d w}{d x} + \rho w' \frac{d}{dx} \frac{d w}{d x}
\end{pmatrix}
\]

where only the mean values, over the space \( S_1 \), of the expressions in the right member are taken into account.

This is the equation for the mean rate, over the space \( S_1 \), of change in the energy of relative-mean-motion per unit of volume.

It may be noticed that the rate of change in the energy of mean-mean-motion, together with the mean rate of change in the energy of relative-mean-motion, must be the total mean-rate of change in the energy of mean-motion, and that by adding the equations (17) and (19) the result is the same as is obtained from the equation (3) of energy of mean-motion by omitting all terms which have no mean value as summed over the space \( S_1 \).

The Expressions from Transformation of Energy from Mean-mean-motion to Relative-mean-motion.

16. When equations (17) and (19) are added together, the only expressions that do not appear in the equation of mean energy of mean-motion are the last terms on the right of each of the equations, which are identical in form and opposite in sign.

These terms which thus represent no change in the total energy of mean-motion can only represent a transformation from energy of mean-mean-motion to energy of relative-mean-motion. And as they are the only expressions which do not form part of the general expression for the rate of change of the mean energy of mean-motion, they represent the total exchange of energy between the mean-mean-motion and the relative-mean-motion.

It is also seen that the action, of which these terms express the effect, is purely
kinematical, depending simply on the instantaneous characters of the mean- and relative-mean-motion, whatever may be the properties of the matter involved, or the mechanical actions which have taken part in determining these characters. The terms, therefore, express the entire result of transformation from energy of mean-mean-motion to energy of relative-mean-motion, and of nothing but the transformation. Their existence thus completely verifies the first of the general conclusions in Art. 14.

The term last but one in the right member of the equation (17) for energy of mean-mean-motion expresses the rate of transformation of energy of heat-motions to that of energy of mean-mean-motion, and is entirely independent of the relative-mean-motion.

In the same way, the term last but one on the right of the equation (19) for energy of relative-mean-motion expresses the rate of transformation from energy of heat-motions to energy of relative-mean-motion, and is quite independent of the mean-mean-motion.

17. In both equations (17) and (19) the first terms on the right express the rates at which the respective energy of mean- and relative-mean-motion are increasing on account of work done by the stresses on the mean- and relative-motion respectively, and by the additions of momentum caused by convections of relative-mean-motion by relative-mean-motion to the mean- and relative-mean-motions respectively.

It may also be noticed that while the first term on the right in the equation (19) of energy of relative-mean-motion is independent of mean-mean-motion, the corresponding term in equation (17) for mean-mean-motion is not independent of relative-mean-motion.

A Discriminating Equation.

18. In integrating the equations over a space moving with the mean-mean-motion of the fluid the first terms on the right may be expressed as surface integrals, which integrals respectively express the rates at which work is being done on, and energy is being received across, the surface by the mean-mean-motion, and by the relative-mean-motion.

If the space over which the integration extends includes the whole system, or such part that the total energy conveyed across the surface by the relative-mean-motion is zero, then the rate of change in the total energy of relative-mean-motion within the space is the difference of the integral, over the space, of the rate of increase of this energy by transformation from energy of mean-mean-motion, less the integral rate at which energy of relative-mean-motion is being converted into heat, or integrating equation (19),
\[
\begin{aligned}
\int\int\int \left( \frac{d}{dt} + \hat{u} \frac{d}{dx} + \hat{v} \frac{d}{dy} + \hat{w} \frac{d}{dz} \right) \mathbf{E} \, dx \, dy \, dz =
\end{aligned}
\]

\[
- \int\int\int \left\{ \rho \hat{u} \frac{d\hat{u}}{dx} + \rho \hat{v} \frac{d\hat{v}}{dy} + \rho \hat{w} \frac{d\hat{w}}{dz} \right\} dx \, dy \, dz
\]

\[
+ \int\int\int \left\{ \rho \hat{v} \frac{d\hat{v}}{dx} + \rho \hat{w} \frac{d\hat{w}}{dy} + \rho \hat{w} \frac{d\hat{w}}{dz} \right\} dx \, dy \, dz
\]

\[
+ \int\int\int \left\{ \frac{\hat{p}_{xx}}{\partial x} + \frac{\hat{p}_{yx}}{\partial y} + \frac{\hat{p}_{zz}}{\partial z} \right\} dx \, dy \, dz
dx \, dy \, dz
\]

\[
+ \int\int\int \left\{ \frac{\hat{p}_{zx}}{\partial x} + \frac{\hat{p}_{yy}}{\partial y} + \frac{\hat{p}_{yy}}{\partial z} \right\} dx \, dy \, dz
\]

This equation expresses the fundamental relations:—

(1) That the only integral effect of the mean-mean-motion on the relative-mean-motion is the integral of the rate of transformation from energy of mean-mean-motion to energy of relative-mean-motion.

(2) That, unless relative energy is altered by actions across the surface within which the integration extends, the integral energy of relative-mean-motion will be increasing or diminishing according as the integral rate of transformation from mean-mean-motion to relative-mean-motion is greater or less than the rate of conversion of the energy of relative-mean-motion into heat.

19. For \( \hat{p}_{xx}, \) &c., are substituted their values as determined according to the theory of viscosity, the approximate truth of which has been verified, as already explained.

Putting

\[
\frac{\hat{p}_{xx}}{\partial x} = \hat{p} + \frac{3}{2} \mu \left( \frac{d\hat{u}}{dx} + \frac{d\hat{v}}{dy} + \frac{d\hat{w}}{dz} \right) - 2 \mu \frac{d\hat{u}}{dx}, \text{ &c., &c.}
\]

\[
\hat{p}_{yx} = - \mu \left( \frac{d\hat{u}}{dy} + \frac{d\hat{v}}{dx} \right), \text{ &c., &c.}
\]

we have, substituting in the last term of equation (20), as the expression for the rate of conversion of energy of relative-mean-motion into heat,

\[
- \int\int\int \hat{p} \frac{d\hat{u}}{dx} + \frac{d\hat{v}}{dy} + \frac{d\hat{w}}{dz} dx \, dy \, dz = \int\int\int \left[ \hat{p} \left( \frac{d\hat{u}}{dx} + \frac{d\hat{v}}{dy} + \frac{d\hat{w}}{dz} \right) \right]
\]

\[
- \mu \left\{ \frac{2}{3} \left( \frac{d\hat{u}}{dx} + \frac{d\hat{v}}{dy} + \frac{d\hat{w}}{dz} \right)^2 \right\} + 2 \left[ \left( \frac{d\hat{u}}{dx} \right)^2 + \left( \frac{d\hat{v}}{dy} \right)^2 + \left( \frac{d\hat{w}}{dz} \right)^2 \right]
\]

\[
+ \left( \frac{d\hat{u}}{dx} \right)^2 + \left( \frac{d\hat{v}}{dy} \right)^2 + \left( \frac{d\hat{w}}{dz} \right)^2 + \left( \frac{d\hat{u}}{dy} \right)^2 + \left( \frac{d\hat{v}}{dy} \right)^2 + \left( \frac{d\hat{w}}{dz} \right)^2 \right\} dx \, dy \, dz . \quad (22)
\]
in which $\mu$ is a function of temperature only; or since $\rho$ is here considered as constant,

\[
-\iiint \frac{d}{dt} \left( \rho H' \right) = -\mu \iiint \left\{ 2 \left[ \left( \frac{\partial w'}{\partial x} \right)^2 + \left( \frac{\partial w'}{\partial y} \right)^2 + \left( \frac{\partial w'}{\partial z} \right)^2 \right] + \left( \frac{\partial w'}{\partial y} + \frac{\partial w'}{\partial x} \right)^2 \right\} dx \, dy \, dz \ldots . \ldots \ (23),
\]

whence substituting for the last term in equation (20) we have, if the energy of relative-mean-motion is maintained, neither increasing or diminishing,

\[
-\rho \iiint \left\{ \frac{\partial u'}{\partial x} \frac{\partial u}{\partial x} + \frac{\partial u'}{\partial y} \frac{\partial u}{\partial y} + \frac{\partial u'}{\partial z} \frac{\partial u}{\partial z} \right\} dx \, dy \, dz \\
+ \frac{\partial v'}{\partial x} \frac{\partial v}{\partial x} + \frac{\partial v'}{\partial y} \frac{\partial v}{\partial y} + \frac{\partial v'}{\partial z} \frac{\partial v}{\partial z} \right\} + \\
\left( \frac{\partial w'}{\partial x} \frac{\partial w}{\partial x} + \frac{\partial w'}{\partial y} \frac{\partial w}{\partial y} + \frac{\partial w'}{\partial z} \frac{\partial w}{\partial z} \right\}
\]

\[
-\mu \iiint \left\{ 2 \left[ \left( \frac{\partial w'}{\partial x} \right)^2 + \left( \frac{\partial w'}{\partial y} \right)^2 + \left( \frac{\partial w'}{\partial z} \right)^2 \right] + \left( \frac{\partial w'}{\partial y} + \frac{\partial w'}{\partial x} \right)^2 \right\} dx \, dy \, dz = 0 \ldots \ldots \ (24),
\]

which is a discriminating equation as to the conditions under which relative-mean-motion can be sustained.

20. Since this equation is homogeneous in respect to the component velocities of the relative-mean-motion, it at once appears that it is independent of the energy of relative-mean-motion divided by the $\rho$. So that if $\mu/\rho$ is constant, the condition it expresses depends only on the relation between variations of the mean-mean-motion and the directional, or angular, distribution of the relative-mean-motion, and on the squares and products of the space periods of the relative-mean-motion.

And since the second term expressing the rate of conversion of heat into energy of relative-mean-motion is always negative, it is seen at once that, whatsoever may be the distribution and angular distribution of the relative-mean-motion and the variations of the mean-mean-motion, this equation must give an inferior limit for the rates of variation of the components of mean-mean-motion, in terms of the limits to the periods of relative-mean-motion, and $\mu/\rho$, within which the maintenance of relative-mean-motion is impossible. And that, so long as the limits to the periods of relative-mean-motion are not infinite, this inferior limit to the rates of variation of the mean-mean-motion will be greater than zero.
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Thus the second conclusion of Art. 14, and the whole of the previous argument is verified, and the properties of matter which prevent the maintenance of mean-motion with periods of the same order of magnitude as those of the heat-motion are shown to be amongst those properties of matter which are included in the equations of motion of which the truth has been verified by experience.

The Cause of Transformation.

21. The transformation function, which appears in the equations of mean-energy of mean- and relative-mean-motion, does not indicate the cause of transformation, but only expresses a kinematical principle as to the effect of the variations of mean-mean-motion, and the distribution of relative-mean-motion. In order to determine the properties of matter and the mechanical principles on which the effect of the variations of the mean-mean-motion on the distribution and angular distribution of relative-mean-motion depends, it is necessary to go back to the equations (16) of relative-momentum at a point; and even then the cause is only to be found by considering the effects of the actions which these equations express in detail. The determination of this cause, though it in no way affects the proofs of the existence of the criterion as deduced from the equations, may be the means of explaining what has been hitherto obscure in the connection between thermodynamics and the principles of mechanics. That such may be the case, is suggested by the recognition of the separate equations of mean- and relative-mean-motion of matter.


22. On consideration, it will at once be seen that there is more than an accidental correspondence between the equations of energy of mean- and relative-mean-motion respectively and the respective equations of energy of mean-motion and of heat in thermodynamics.

If instead of including only the effects of the heat-motion on the mean-momentum as expressed by \( p_{xx} \), &c., the effects of relative-mean-motion are also included by putting \( p_{xx} \) for \( p_{xx} + \rho \omega' \xi' \), &c., and \( p_{yy} \) for \( p_{yy} + \rho \omega' \eta' \), &c., in equations (15) and (17), the equations (15) of mean-mean-motion become identical in form with the equations (1) of mean-motion, and the equation (17) of energy of mean-mean-motion becomes identical in form with the equation (3) of energy of mean-motion.

These equations, obtained from (15) and (17) being equally true with equations (1) and (3), the mean-mean-motion in the former being taken over the space \( S_1 \) instead of \( S_0 \) as in the latter, then, instead of equation (9), we should have for the value of the last term—
\[ P_{xx} \frac{du}{dx} + \Delta c, = - \frac{d(\mu H)}{dt} + u\nu \frac{du}{dx} + \Delta c. \quad \ldots \ldots \quad (25) \]

In which the right member expresses the rate at which heat is converted into energy of mean-mean-motion, together with the rate at which energy of relative-mean-motion is transformed into energy of mean-mean-motion; while equation (19) shows whence the transformed energy is derived.

The similarity of the parts taken by the transformation of mean-mean-motion into relative-mean-motion, and the conversion of mean-motion into heat, indicates that these parts are identical in form; or that the conversion of mean-motion into heat is the result of transformation, and is expressible by a transformation function similar in form to that for relative-mean-motion, but in which the components of relative motion are the components of the heat-motions and the density is the actual density at each point. Whence it would appear that the general equations, of which equations (19) and (16) are respectively the adaptations to the special condition of uniform density, must, by indicating the properties of matter involved, afford mechanical explanations of the law of universal dissipation of energy and of the second law of thermodynamics.

The proof of the existence of a criterion as obtained from the equations is quite independent of the properties and mechanical principles on which the effect of the variations of mean-mean-motion on the distribution of relative mean-motion depends. And as the study of these properties and principles requires the inclusion of conditions which are not included in the equations of mean-motion of incompressible fluid, it does not come within the purpose of this paper. It is therefore reserved for separate investigation by a more general method.

The Criterion of Steady Mean-motion.

23. As already pointed out, it appears from the discriminating equation that the possibility of the maintenance of a state of relative-mean-motion depends on \( \mu/\rho \), the variation of mean-mean-motion and the periods of the relative-mean-motion.

Thus, if the mean-mean-motion is in direction \( x \) only, and varies in direction \( y \) only, if \( u', v', w' \) are periodic in directions \( x, y, z \), \( a \) being the largest period in space, so that their integrals over a distance \( \alpha \) in direction \( x \) are zero, and if the co-efficients of all the periodic factors are \( \alpha \), then putting

\[ \pm d\bar{u}/dy = C^3_1; \]

taking the integrals, over the space \( a^3 \) of the 18 squares and products in the last term on the left of the discriminating equation (24) to be
the integral of the first term over the same space cannot be greater than

\[ \rho C_2 \alpha^3 C_1^2 a^3. \]

Then, by the discriminating equation, if the mean-energy of relative-mean-motion is to be maintained,

\[ \rho C_1^2 \text{ is greater than } 700 \mu/a^2, \]

or

\[ \frac{\rho \alpha^2}{\mu} \sqrt{\left(\frac{du}{dy}\right)^2} = 700. \]

is a condition under which relative-mean-motion cannot be maintained in a fluid of which the mean-mean-motion is constant in the direction of mean-mean-motion, and subject to a uniform variation at right angles to the direction of mean-mean-motion. It is not the actual limit, to obtain which it would be necessary to determine the actual forms of the periodic function for \( u', v', w' \), which would satisfy the equations of motion (15), (16), as well as the equation of continuity (13), and to do this the functions would be of the form

\[ \sum \left[ A_r \cos \left\{ r \left( nt + \frac{2\pi}{\alpha} x \right) \right\} \right], \]

where \( r \) has the values 1, 2, 3, &c. It may be shown, however, that the retention of the terms in the periodic series in which \( r \) is greater than unity would increase the numerical value of the limit.

24. It thus appears that the existence of the condition (26) within which no relative-mean-motion, completely periodic in the distance \( \alpha \), can be maintained, is a proof of the existence, for the same variation of mean-mean-motion, of an actual limit of which the numerical value is between 700 and infinity.

In viscous fluids, experience shows that the further kinematic conditions imposed by the equations of motion do not prevent such relative-mean-motion. Hence for such fluids equation (26) proves the actual limit, which discriminates between the possibility and impossibility of relative-mean-motion completely periodic in a space \( a \), is greater than 700.

Putting equation (26) in the form

\[ \sqrt{(du/\gamma)^2} = 700 \mu/\rho a^2, \]

it at once appears that this condition does not furnish a criterion as to the possibility of the maintenance of relative-mean-motion, irrespective of its periods, for a certain condition of variation of mean-mean-motion. For by taking \( \alpha^2 \) large enough, such relative-mean-motion would be rendered possible whatever might be the variation of the mean-mean-motion.
The existence of a criterion is thus seen to depend on the existence of certain restrictions to the value of the periods of relative-mean-motion—on the existence of conditions which impose superior limits on the values of \( \alpha \).

Such limits to the maximum values of \( \alpha \) may arise from various causes. If \( d\alpha/dy \) is periodic, the period would impose such a limit, but the only restrictions which it is my purpose to consider in this paper, are those which arise from the solid surfaces between which the fluid flows. These restrictions are of two kinds—restrictions to the motions normal to the surfaces, and restrictions tangential to the surfaces—the former are easily defined, the latter depend for their definition on the evidence to be obtained from experiments such as those of Poiseuille, and I shall proceed to show that these restrictions impose a limit to the value of \( \alpha \), which is proportional to \( D \), the dimension between the surfaces. In which case, if

\[
\sqrt{(d\alpha/dy)^2} = U/D,
\]

equation (26) affords a proof of the existence of a criterion

\[
\rho DU/\mu = K 
\]

of the conditions of mean-mean-motion under which relative or sinuous-motion can continuously exist in the case of a viscous fluid between two continuous surfaces perpendicular to the direction \( y \), one of which is maintained at rest, and the other in uniform tangential-motion in the direction \( x \) with velocity \( U \).

Section III.

The Criterion of the Conditions under which Relative-mean-motion cannot be maintained in the case of Incompressible Fluid in Uniform Symmetrical Mean-flow between Parallel Solid Surfaces.—Expression for the Resistance.

25. The only conditions under which definite experimental evidence as to the value of the criterion has as yet been obtained are those of steady flow through a straight round tube of uniform bore; and for this reason it would seem desirable to choose for theoretical application the case of a round tube. But inasmuch as the application of the theory is only carried to the point of affording a proof of the existence of an inferior limit to the value of the criterion which shall be greater than a certain quantity determined by the density and viscosity of the fluid and the conditions of flow, and as the necessary expressions for the round tube are much more complex than those for parallel plane surfaces, the conditions here considered are those defined by such surfaces.
Fluids and the Determination of the Criterion.

Case I. Conditions.

26. The fluid is of constant density $\rho$ and viscosity $\mu$, and is caused to flow, by a uniform variation of pressure $d\bar{p}/dx$, in direction $x$ between parallel surfaces, given by

$$y = -b_0, \quad y = b_0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (28),$$

the surfaces being of indefinite extent in directions $z$ and $x$.

The Boundary Conditions.

1.) There can be no motion normal to the solid surfaces, therefore

$$v = 0 \text{ when } y = \pm b_0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (29).$$

2.) That there shall be no tangential motion at the surface, therefore

$$u = w = 0 \text{ when } y = \pm b_0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (30);$$

whence by equation (21), putting $u$ for $u'$, $p_{yx} = -\mu du/dy$.

By the equation of continuity $du/dx + dv/dy + dw/dz = 0$, therefore at the boundaries we have the further conditions, that when $y = \pm b_0$,

$$du/dx = dv/dy = dw/dz = 0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (31).$$

Singular Solution.

27. If the mean-motion is everywhere in direction $x$, then, by the equation of continuity, it is constant in this direction, and as shown (Art. 8) the periods of mean-motion are infinite, and the equations (1), (3), and (9) are strictly true. Hence if

$$\bar{v} = w = u' = v' = w' = 0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (32),$$

we have conditions under which a singular solution of the equations, applied to this case, is possible whatsoever may be the value of $b_0$, $d\bar{p}/dx$, $\rho$ and $\mu$.

Substituting for $p_{xx}, p_{yy}, \&c.$, in equations (1) from equations (21), and substituting $u$ for $u', \&c.$, these become

$$\rho \frac{du}{dt} = -\frac{d\bar{p}}{dx} + \mu \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (33).$$
This equation does not admit of solution from a state of rest;* but assuming a condition of steady motion such that \(du/dt\) is everywhere zero, and \(dp/dx\) constant, the solution of

\[
\frac{\mu}{\rho} \left( \frac{d^2u}{dy^2} + \frac{d^2u}{dz^2} \right) - \frac{1}{\rho} \frac{dp}{dx} = 0,
\]

if

\[
u = du/dz = 0 \quad \text{when} \quad y = \pm b_o,
\]

is

\[
u = \frac{1}{\mu} \frac{dp}{dx} \frac{y^2 - b_o^2}{2}
\]

This is a possible condition of steady motion in which the periods of \(u\) according to Art. 8 are infinite; so that the equations for mean-motion as affected by heat-motion, by Art. 8, are exact, whatever may be the values of

\(u, b_o, \rho, \mu, \) and \(dp/dx\).

The last of equations (34) is thus seen to be a singular solution of the equations (15) for steady mean-flow, or steady mean-mean-motion, when \(u', v', w', p', \&c.,\) have severally the values zero, and so the equations (16) of relative-mean-motion are identically satisfied.

In order to distinguish the singular values of \(u, I\) put

\[u = U, \quad \int_{-b}^{b} u \, dy = 2b_o U_m; \]

whence

\[
\frac{dp}{dx} = - \frac{3\mu}{b_o^3} U_m, \quad U = \frac{3}{2} U_m \frac{b_o^2 - y^2}{b_o^3}
\]

According to the equations such a singular solution is always possible where the conditions can be realized, but the manner in which this solution of the equation (1) of mean-motion is obtained affords no indication as to whether or not it is the only solution—as to whether or not the conditions can be realized. This can only be ascertained either by comparing the results as given by such solutions with the results obtained by experiment, or by observing the manner of motion of the fluid, as in my experiments with colour bands.

* In a paper on the "Equations of Motion and the Boundary Conditions of Viscous Fluid," read before Section A at the meeting of the B.A., 1883, I pointed out the significance of this disability to be integrated, as indicating the necessity of the retention of terms of higher orders to complete the equations, and advanced certain confirmatory evidence as deduced from the theory of gases. The paper was not published, as I hoped to be able to obtain evidence of a more definite character, such as that which is now adduced in Articles 7 and 8 of this paper, which shows that the equations are incomplete, except for steady motion, and that to render them integrable from rest the terms of higher orders must be retained, and thus confirms the argument I advanced, and completely explains the anomaly.
FLUIDS AND THE DETERMINATION OF THE CRITERION.

The fact that these conditions are realized, under certain circumstances, has afforded the only means of verifying the truth of the assumptions as to the boundary conditions, that there shall be no slipping, and as to \( \mu \) being independent of the variations of mean-motion.

**Verification of the Assumptions in the Equation of Viscous Fluid.**

28. As applied to the conditions of Poiseuille's experiments and similar experiments made since, the results obtained from the theory are found to agree throughout the entire range so long as \( u', v', w' \) are zero, showing that if there were any slipping it must have been less than the thousandth part of the mean flow, although the tangential force at the boundary was 0.2 gr. per square centimetre, or over 6 lbs. per square foot, the mean flow 376 millims. (1.23 feet) per second, and

\[
\frac{du}{dr} = 215,000,
\]

the diameter of this tube being 0.014 millim., the length 125 millims., and the head 30 inches of mercury.

Considering that the skin resistance of a steamer going at 25 knots is not 6 lbs. per square foot, it appears that the assumptions as to the boundary conditions and the constancy of \( \mu \) have been verified under more exigent circumstances, both as regards tangential resistance and rate of variation of tangential stress, than occur in anything but exceptional cases.

**Evidence that other Solutions are possible.**

29. The fact that steady mean-motion is almost confined to capillary tubes—and that in larger tubes, except when the motion is almost insensibly slow, the mean-motion is sinuous and full of eddies, is abundant evidence of the possibility, under certain conditions, of solutions other than the singular solutions.

In such solutions \( u', v', w' \) have values, which are maintained, not as a system of steady periodic motion, but such as has a steady effect on the mean flow through the tube; and equations (1) are only approximately true.

**The Application of the Equations of the Mean- and Relative-mean-motion.**

30. Since the components of mean-mean-motion in directions \( y \) and \( z \) are zero, and the mean flow is steady,

\[
\bar{v} = 0, \quad \bar{w} = 0, \quad \frac{du}{dt} = 0, \quad \frac{du}{dx} = 0 \quad \ldots \quad (36),
\]
and as the mean values of functions of \( u', v', w' \) are constant in the direction of flow,
\[
\frac{d}{dx} \left( \frac{u' w'}{dx} \right) = 0, \quad \frac{d}{dx} \left( \frac{v' w'}{dx} \right) = 0, \quad \frac{d}{dx} \left( \frac{w' w'}{dx} \right) = 0, \&c. \quad \ldots \ldots (37).
\]

By equations (21) and (37) the equations (15) of mean-motion become
\[
\begin{align*}
\rho \frac{d\bar{u}}{dt} &= - \frac{dp}{dx} + \mu \left( \frac{d^2u}{dy^2} + \frac{d^2u}{dz^2} \right) - \rho \left\{ \frac{d}{dy} (u' v') + \frac{d}{dz} (u' w') \right\} \\
\rho \frac{d\bar{v}}{dt} &= - \frac{dp}{dy} - \rho \left\{ \frac{d}{dy} (v' v') + \frac{d}{dz} (v' w') \right\} \\
\rho \frac{d\bar{w}}{dt} &= - \frac{dp}{dz} - \rho \left\{ \frac{d}{dy} (w' v') + \frac{d}{dz} (w' w') \right\}
\end{align*}
\]

The equation of energy of mean-motion (17) becomes
\[
\frac{d(E)}{dt} = - \bar{u} \frac{dp}{dx} + \mu \left\{ \frac{d}{dy} \left( \frac{u}{dy} \right) + \frac{d}{dz} \left( \frac{u}{dz} \right) \right\} - \rho \left\{ \frac{d}{dy} (\bar{u} v') + \frac{d}{dz} (\bar{u} w') \right\} \\
- \mu \left\{ \left( \frac{du}{dy} \right)^2 + \left( \frac{du}{dz} \right)^2 \right\} + \rho \left\{ \bar{u} v' \frac{du}{dy} + \bar{u} w' \frac{du}{dz} \right\}
\]

Similarly the equation of mean-energy of relative-mean-motion (19) becomes
\[
\frac{d\bar{E}'}{dt} = - \frac{d}{dy} \left[ \bar{u}' (p'_{zz} + \bar{u}' v') + v' (p'_{zz} + \bar{v}' v') + w' (p'_{zz} + \bar{w}' v') \right] \\
- \frac{d}{dz} \left[ u' (p'_{zz} + \bar{u}' v') + v' (p'_{zz} + \bar{v}' v') + w' (p'_{zz} + \bar{w}' v') \right] \\
- \mu \left\{ 2 \left( \frac{d\bar{u}'}{dx} \right)^2 + \left( \frac{d\bar{v}'}{dy} \right)^2 + \left( \frac{d\bar{w}'}{dz} \right)^2 \right\} + \left( \frac{d\bar{w}'}{dy} + \frac{d\bar{v}'}{dz} \right)^2 + \left( \frac{d\bar{v}'}{dx} + \frac{d\bar{w}'}{dz} \right)^2 \\
- \rho \left\{ \bar{u} v' \frac{d\bar{u}'}{dy} + \bar{u} w' \frac{d\bar{u}'}{dz} \right\}
\]

Integrating in directions \( y \) and \( z \) between the boundaries and taking note of the boundary conditions by which \( \bar{u}, u', v', w' \) vanish at the boundaries together with the integrals, in direction \( z \), of
\[
\frac{d}{dz} \left( \frac{-du}{dz} \right), \quad \frac{d}{dz} \left[ u \left( \bar{u} w' \right) \right], \quad \frac{d}{dz} \left[ u' \left( p_{zz} + \bar{u} w' \right) \right], \&c.,
\]
the integral equation of energy of mean-motion becomes
\[
\left[ \int \frac{dE}{dt} \, dy \right] dz = - \left[ \int \left\{ \frac{-dp}{dx} + \mu \left\{ \left( \frac{du}{dy} \right)^2 + \left( \frac{du}{dz} \right)^2 \right\} - \rho \left\{ \bar{u} v' \frac{du}{dy} + \bar{u} w' \frac{du}{dz} \right\} \right\} \, dy \right] dz. \quad (41)
\]
The integral equation of energy of relative-mean-motion becomes

\[
\int \frac{dE'}{dt} dy dz = - \int \left[ \rho \left( \frac{u'v' \, du}{dy} + \frac{u'w' \, dw}{dz} \right) \right] dy dz - \mu \int \left[ 2 \left( \frac{dw'}{dx} \right)^2 + \left( \frac{dv'}{dy} \right)^2 \right. \\
+ \left( \frac{dv'}{dx} + \frac{dv'}{dy} \right)^2 + \left( \frac{du'}{dx} + \frac{du'}{dy} \right)^2 \left( \frac{du'}{dx} + \frac{du'}{dy} \right) \right] dy dz \quad \ldots \quad (42).
\]

If the mean-mean-motion is steady it appears from equation (41) that

\[
- \int u \frac{d\rho}{dx} dy dz,
\]

the work done on the mean-mean-motion \( \bar{u} \), per unit of length of the tube, by the constant variation of pressure, is in part transformed into energy of relative-mean-motion at a rate expressed by the transformation function

\[
- \int \rho \left( \frac{u'v' \, du}{dy} + \frac{u'w' \, dw}{dy} \right) dy dz,
\]

and in part transformed into heat at the rate

\[
\mu \int \left[ 2 \left( \frac{dw'}{dx} \right)^2 + \left( \frac{dv'}{dy} \right)^2 \right] dy dz.
\]

While the equation (42) for the integral energy of relative-mean-motion shows that the only energy received by the relative-mean-motion is that transformed from mean-mean-motion, and the only energy lost by relative-mean-motion is that converted into heat by the relative-mean-motion at the rate expressed by the last term.

And hence if the integral of \( E' \) is maintained constant, the rate of transformation from energy of mean-mean-motion must be equal to the rate at which energy of relative-mean-motion is converted into heat, and the discriminating equation becomes

\[
\int \rho \left( \frac{u'v' \, du}{dy} + \frac{u'w' \, dw}{dz} \right) dy dz = - \mu \int \left[ 2 \left( \frac{dw'}{dx} \right)^2 + \left( \frac{dv'}{dy} \right)^2 \right. \\
+ \left( \frac{dv'}{dz} + \frac{du'}{dy} \right)^2 + \left( \frac{du'}{dz} + \frac{du'}{dy} \right)^2 \left( \frac{du'}{dz} + \frac{du'}{dy} \right) \right] dy dz \quad . (43).
\]

The Conditions to be Satisfied by \( \bar{u} \) and \( u', v', w' \).

31. If the mean-mean-motion is steady \( \bar{u} \) must satisfy:—

\[
x \, 2
\]
(1) The boundary conditions
\[ \bar{u} = 0 \text{ when } y = \pm b_0 \] (44);

(2) The equation of continuity
\[ d\bar{u}/dx = 0 \] (45);

(3) The first of the equations of motion (38)
\[ \frac{d\rho}{dz} = \mu \left( \frac{d\bar{u}}{dy} \right)^2 + \frac{d\bar{u}}{dz^2} - \rho \left\{ \frac{d}{dy} \left( u'v' \right) + \frac{d}{dz} \left( \bar{u}\bar{w} \right) \right\} \] (46); or putting,
\[ \bar{u} = U + \bar{u} - U \text{ and } d\rho/dx = \mu d^2U/dy^2 \]
as in the singular solution, equation (46) becomes
\[ \mu \left( \frac{d^2(\bar{u} - U)}{dy^2} + \frac{d^2(\bar{u} - U)}{dz^2} \right) = \rho \left\{ \frac{d}{dy} \left( u'v' \right) + \frac{d}{dz} \left( \bar{u}\bar{w} \right) \right\} \] (47);

(4) The integral of (47) over the section of which the left member is zero, and
the mean value of \( \mu d\bar{u}/dy = \mu dU/dy \) when \( y = \pm b_0 \) . . . (48).

From the condition (3) it follows that if \( \bar{u} \) is to be symmetrical with respect to the boundary surfaces, the relative-mean-motion must extend throughout the tube, so that
\[ \int_{-\infty}^{\infty} \left( \frac{d\bar{u}v'}{dy} + \frac{d\bar{u}'w'}{dz} \right) dz \text{ is a function of } y^2 . . . . . . . . (49). \]

And as this condition is necessary, in order that the equations (38) of mean-mean-motion and the equations (16) of relative-mean-motion may be satisfied for steady mean-motion, it is assumed as one of the conditions for which the criterion is sought.

The components of relative-mean-motion must satisfy the periodic conditions as expressed in equations (12), which become, putting \( 2c \) for the limit in direction \( z \),
\[ \int_{-c}^{c} u' dx = \int_{-c}^{c} v' dx = \int_{-c}^{c} w' dx = 0 \] (50).

(2) The equation of continuity
\[ du'/dx + dv'/dy + dw'/dz = 0. \]
(3) The boundary conditions which with the continuity give

\[ u' = v' = w' = du'/dx = dv'/dy = dw'/dz = 0 \text{ when } y = \pm b \quad (51). \]

(4) The condition imposed by symmetrical mean-motion

\[ \int_{-\varepsilon}^{\varepsilon} \left( \frac{du'x'}{dy} + \frac{du'w'}{dz} \right) dz = 2cf(y^2) \quad \ldots \ldots \ldots (52). \]

These conditions (1 to 4) must be satisfied if the effect on \( \tilde{u} \) is to be symmetrical however arbitrarily \( u', v', w' \) may be superimposed on the mean-motion which results from a singular solution.

(5) If the mean-motion is to remain steady \( u', v', w' \) must also satisfy the kinematical conditions obtained by eliminating \( p \) from the equations of mean-mean-motion (33) and those obtained by eliminating \( p' \) from the equations of relative-mean-motion (16).

*Conditions (1 to 4) determine an inferior Limit to the Criterion.*

32. The determination of the kinematic conditions (5) is, however, practically impossible; but if they are satisfied, \( u', v', w' \) must satisfy the more general conditions imposed by the discriminating equation. From which it appears that when \( u', v', w' \) are such as satisfy the conditions (1 to 4), however small their values relative to \( \tilde{u} \) may be, if they be such that the rate of conversion of energy of relative-mean-motion into heat is greater than the rate of transformation of energy of mean-mean-motion into relative-mean-motion, the energy of relative-mean-motion must be diminishing. Whence, when \( u', v', w' \) are taken such periodic functions of \( x, y, z \), as under conditions (1 to 4) render the value of the transformation function relative to the value of the conversion function a maximum, if this ratio is less than unity, the maintenance of any relative-mean-motion is impossible. And whatever further restrictions might be imposed by the kinematical conditions, the existence of an inferior limit to the criterion is proved.

*Expressions for the Components of possible Relative-mean-motion.*

33. To satisfy the first three of the equations (50) the expressions for \( u', v', w' \), must be continuous periodic functions of \( x \), with a maximum periodic distance \( \alpha \), such as satisfy the conditions of continuity.

Putting

\[ l = 2\pi/\alpha \; \text{and} \; n \; \text{for any number from 1 to } \infty, \]
and
\[ u' = \Sigma_o \left\{ \left( \frac{d\alpha}{dy} + \frac{d\gamma}{dz} \right) \cos (nlx) + \left( \frac{d\theta}{dy} + \frac{d\delta}{dz} \right) \sin (nlx) \right\} \]
\[ v' = \Sigma_o \left\{ n\alpha \sin (nlx) - n\beta \cos (nlx) \right\} \]
\[ w' = \Sigma_o \left\{ n\gamma \sin (nlx) - n\delta \cos (nlx) \right\} \]

\[ u', v', w' \] satisfy the equation of continuity. And, if
\[ \alpha = \beta = \gamma = \delta = d\alpha/dy = d\beta/dy = d\gamma/dz = d\delta/dz = 0 \text{ when } y = \pm b \]
and \( \alpha \beta, \alpha \gamma, \alpha \delta \) are all functions of \( y \) only

it would seem that the expressions are the most general possible for the components of relative-mean-motion.

**Cylindrical-relative-motion.**

34. If the relative-mean-motion, like the mean-mean-motion, is restricted to motion parallel to the plane of \( xy \),
\[ \gamma = \delta = \omega' = 0, \text{ everywhere,} \]
and the equations (53) express the most general forms for \( u', v' \) in case of such cylindrical disturbance.

Such a restriction is perfectly arbitrary, and having regard to the kinematical restrictions, over and above those contained in the discriminating equation, would entirely change the character of the problem. But as no account of these extra kinematical restrictions is taken in determining the limit to the criterion, and as it appears from trial that the value found for this limit is essentially the same, whether the relative-motion is general or cylindrical, I only give here the considerably simpler analyses for the cylindrical motion.

**The Functions of Transformation of Energy and Conversion to Heat for Cylindrical Motion.**

35. Putting
\[ \frac{d}{dt} (\mu H) \]
for the rate at which energy of relative-mean-motion is converted to heat per unit of volume, expressed in the right-hand member of the discriminating equation (43),
\[ \int \int \int \frac{d}{dt} (\mu H) \, dx \, dy \, dz \]
\[ = \mu \int \int \int \left\{ 2 \left[ \left( \frac{dv'}{dx} \right)^2 + \left( \frac{dv'}{dy} \right)^2 \right] + \left( \frac{dw'}{dx} \right)^2 + \left( \frac{dw'}{dy} \right)^2 + 2 \frac{dw'}{dy} \frac{dw'}{dx} \right\} \, dx \, dy \, dz \quad . \quad (56). \]
Then substituting for the values of \( u', v', w' \) from equations (53), and integrating in direction \( x \) over \( 2\pi/l \), and omitting terms the integral of which, in direction \( y \), vanishes by the boundary conditions,

\[
\left[ \int \frac{d}{dt} \left( \mu H' \right) dy \right] dz = \frac{\mu}{2} \left[ \int \Sigma \left\{ (nl)^4 \left( \alpha_x^2 + \beta_x^2 \right) + 2 \left( \frac{d\alpha_x}{dy} \right)^2 + \left( \frac{d\beta_x}{dy} \right)^2 \right\} dy \right] dz.
\]

In a similar manner, substituting for \( u' \), integrating, and omitting terms which vanish on integration, the rate of transformation of energy from mean-mean-motion, as expressed by the left member in the discriminating equation (43), becomes

\[
\left[ \int \rho \frac{\partial}{\partial y} \left( \frac{\partial u'}{\partial y} \right) dy \right] dz = \frac{1}{2} \left[ \int \Sigma \left\{ nl \left( \alpha_x \frac{d\beta_x}{dy} - \beta_x \frac{d\alpha_x}{dy} \right) \right\} dy \right] dz.
\]

And, since by Art. 31, conditions (3) equation (47),

\[
\mu \frac{d}{dy} (\bar{u} - U) = \rho \frac{d}{dy} (\bar{v} \bar{v}) \quad \ldots \quad (59),
\]

integrating and remembering the boundary conditions,

\[
\mu \frac{d}{dy} (\bar{u} - U) = \rho \bar{v} \bar{v}, \quad \mu (\bar{u} - U) = \rho \left[ \bar{v} \bar{v} \right] dy \quad \ldots \quad (60).
\]

And since at the boundary \( \bar{u} - U \) is zero,

\[
\rho \int_{-b_0}^{b_0} (\bar{u} \bar{v}) dy = 0 \quad \ldots \quad (61).
\]

Whence, putting \( U + \bar{u} - U \) for \( \bar{u} \) in the right member of equation (58), substituting for \( \bar{u} - U \) from (60), integrating by parts, and remembering that

\[
\frac{d^2 U}{dy^2} = -3 \frac{\partial U}{\partial y}, \quad \text{which is constant} \quad \ldots \quad (62),
\]

also that

\[
\bar{u} \bar{v}' = \frac{1}{2} \Sigma \left\{ nl \left( \alpha_x \frac{d\beta_x}{dy} - \beta_x \frac{d\alpha_x}{dy} \right) \right\} \quad \ldots \quad (63),
\]

we have for the transformation function

\[
\int_{-b_0}^{b_0} \left( \rho \bar{u} \bar{v} \frac{du}{dy} \right) dy
\]

\[
= \Sigma \left[ \frac{3}{2} \rho \frac{U_m}{b_0^3} \int_{-b_0}^{b_0} \left( \alpha_x \frac{d\beta_x}{dy} - \beta_x \frac{d\alpha_x}{dy} \right) dy + \frac{\rho^3}{4\mu} \int_{-b_0}^{b_0} (nl)^2 \left( \alpha_x \frac{d\beta_x}{dy} - \beta_x \frac{d\alpha_x}{dy} \right)^2 dy \right].
\]

\[
(64).
\]
If \( u', v' \) are indefinitely small the last term, which is of the fourth degree, may be neglected.

Substituting in the discriminating equation (43) this may be put in the form

\[
\frac{2\rho b_0 U_m}{\mu} = 2b_0^3 \int_{-b_0}^{b_0} \left\{ n^4 P^2 (\alpha_u \beta_u + \beta_u \alpha_u) + 2n^2 \left[ \left( \frac{d\alpha_u}{dy} \right)^2 + \left( \frac{d\beta_u}{dy} \right)^2 \right] + \left( \frac{d^2\alpha_u}{dy^2} \right)^2 + \left( \frac{d^2\beta_u}{dy^2} \right)^2 \right\} dy \tag{65}
\]

Limits to the Periods.

36. As functions of \( y \) the variations of \( \alpha_u, \beta_u \) are subject to the restrictions imposed by the boundary conditions, and in consequence their periodic distances are subject to superior limits determined by \( 2b_0 \), the distance between the fixed surfaces.

In direction \( x \), however, there is no such direct connection between the value of \( b_0 \) and the limits to the periodic distance, as expressed by \( 2\pi nl \). Such limits necessarily exist, and are related to the limits of \( \alpha_u, \beta_u \) in consequence of the kinemetical conditions necessary to satisfy the equations of motion for steady mean-mean-motion; these relations, however, cannot be exactly determined without obtaining a general solution of the equations.

But from the form of the discriminating equation (43) it appears that no such exact determination is necessary in order to prove the inferior limit to the criterion.

The boundaries impose the same limits on \( \alpha_u, \beta_u \) whatever may be the value of \( nl \); so that if the values of \( \alpha_u, \beta_u \) be determined so that the value of

\[
\frac{2\rho b_0 U_m}{\mu}
\]

is a minimum for every value of \( nl \), the value of \( rl \), which renders this minimum a minimum-minimum may then be determined, and so a limit found to which the value of the complete expression approaches, as the series in both numerator and denominator become more convergent for values of \( nl \) differing in both directions from \( rl \).

Putting \( l, \alpha, \beta \) for \( rl, \alpha_u, \beta_u \) respectively, and putting for the limiting value to be found for the criterion

\[
K_1 = \frac{2\rho b_0 U_m}{\mu} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (66)
\]

\[
\frac{3}{2} K_1 = b_0^3 \int_{-b_0}^{b_0} \left\{ 3 \left( \frac{d\alpha_u}{dy} \right)^2 + 2n^2 \left[ \left( \frac{d\beta_u}{dy} \right)^2 + \left( \frac{d^2\alpha_u}{dy^2} \right)^2 + \left( \frac{d^2\beta_u}{dy^2} \right)^2 \right] \right\} dy 
+ l \int_{-b_0}^{b_0} dy \int_{-b_0}^{b_0} \left( \frac{d\beta_u}{dy} - \frac{d\alpha_u}{dy} \right) dy \tag{67}
\]

when \( \alpha \) and \( \beta \) are such functions of \( y \) that \( K_1 \) is a minimum whatever the value of \( l \), and \( l \) is so determined as to render \( K_1 \) a minimum-minimum.
Having regard to the boundary conditions, &c., and omitting all possible terms which increase the numerator without affecting the denominator, the most general form appears to be

\[ \alpha = \sum_0^\infty \left[ a_{2s+1} \sin (2s+1)p \right], \]

\[ \beta = \sum_0^\infty \left[ b_{2t} \sin (2tp) \right], \]

where

\[ \rho = \pi y/2b_0 \]

(68).

To satisfy the boundary conditions

- \( s = 2r \), when \( s \) is even,
- \( s = 2r + 1 \), when \( s \) is odd.
- \( t = 2r + 1 \), when \( t \) is odd,
- \( t = 2(r + 1) \), when \( t \) is even.

Since \( \alpha = 0 \), when \( p = \pm \frac{1}{2}\pi \),

\[ \sum_0^\infty (a_{2r+1} - a_{2r+3}) = 0, \]

and since \( d\beta/dy = 0 \), when \( p = \pm \frac{1}{2}\pi \),

\[ \sum_0^\infty \{- (4r + 2) b_{2r+2} + 4(r + 1) b_{2r+4} \} = 0 \]

(69).

From the form of \( K \) it is clear that every term in the series for \( \alpha \) and \( \beta \) increases the value of \( K \) and to an extent depending on the value of \( r \). \( K \) will therefore be minimum, when

\[ \alpha = a_1 \sin p + a_3 \sin 3p \]

\[ \beta = b_2 \sin 2p + b_4 \sin 4p \]

(70),

which satisfy the boundary conditions if

\[ \begin{align*}
  a_3 &= a_1 \\
  b_2 &= 2b_4
\end{align*} \]

(71).

Therefore we have, as the values of \( \alpha \) and \( \beta \), which render \( K \) a minimum for any value of \( l \)

\[ \frac{\alpha}{a_1} = \sin p + \sin 3p, \quad \frac{\beta}{b_2} = \sin 2p + \frac{1}{2} \sin 4p. \]

And

\[ \begin{align*}
  \frac{2b_0}{\pi a_1} \frac{d\alpha}{dy} &= \cos p + 3 \cos 3p, \\
  \frac{2b_0}{\pi b_2} \frac{d\beta}{dy} &= 2 \cos 2p + 2 \cos 4p, \\
  \frac{2b_0}{\pi a_1 b_2} \left( \frac{d\beta}{dy} - \frac{2}{3} \frac{d\alpha}{dy} \right) &= \frac{1}{4} \left( -3 \sin p - 3 \sin 3p + \sin 5p + \sin 7p \right)
\end{align*} \]

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and integrating twice

\[ \int_{-b_0}^{b_0} dy \int_{-b_0}^{b_0} \left( \frac{d\beta}{dy} - \frac{d\alpha}{dy} \right) dy = -1.325 \frac{l}{\pi} \frac{2b_0}{a_1 b_2} \quad \ldots \quad (73). \]

Putting

\[ \frac{\pi}{2b_0} L \text{ for } l, \]

the denominator of \( \frac{3}{2} K_1 \), equation (67), becomes

\[ -1.325 L a_1 b_2. \]

In a similar manner the numerator is found to be

\[ b_0^4 \left( \frac{\pi}{2b_0} \right)^4 \left\{ L^4 (2a_1^2 + 1.25b_2^2) + 2L^2 (10a_1^2 + 8b_2^2) + 8a_1^2 + 8b_2^2 \right\}, \]

and as the coefficients of \( a_1 \) and \( b_2 \) are nearly equal in the numerator, no sensible error will be introduced by putting

\[ b_2 = -a_1, \]

then

\[ \frac{3}{2} K_1 = \frac{L^4 + 2 \times 5.33L^2 + 50 \left( \frac{\pi}{2} \right)^4}{0.408L} \quad \ldots \quad (74) \]

which is a minimum if

\[ L = 1.62 \quad \ldots \quad (75) \]

and

\[ K_1 = 517 \quad \ldots \quad (76). \]

Hence, for a flat tube of unlimited breadth, the criterion

\[ \rho 2b_0 U_0/\mu \text{ is greater than } 517 \quad \ldots \quad (77). \]

37. This value must be less than that of the criterion for similar circumstances. How much less it is impossible to determine theoretically without effecting a general solution of the equations; and, as far as I am aware, no experiments have been made in a flat tube. Nor can the experimental value 1000, which I obtained for the round tube, be taken as indicative of the value for a flat tube, except that, both theoretically and practically, the critical value of \( U_0 \) is found to vary inversely as the hydraulic mean depth, which would indicate that, as the hydraulic mean depth in a flat tube is double that for a round tube, the criterion would be half the value, in which case the limit found for \( K_1 \) would be about 0.61 \( K \). This is sufficient to show that the absolute theoretical limit found is of the same order of magnitude as the experimental
value; so that the latter verifies the theory, which, in its turn, affords an explanation of the observed facts.

The State of Steady Mean-motion above the Critical Value.

38. In order to arrive at the limit for the criterion it has been necessary to consider the smallest values of \( v', v, w' \), and the terms in the discriminating equation of the fourth degree have been neglected. This, however, is only necessary for the limit, and, preserving these higher terms, the discriminating equation affords an expression for the resistance in the case of steady mean-mean-motion.

The complete value of the function of transformation as given in equation (64) is

\[
\int_{-b_0}^{b_0} \left( \rho \underline{v}' v' \frac{d\underline{v}}{dy} \right) dy = \sum \left[ \rho \frac{3U_n}{2b_0^3} \int_{-b_0}^{b_0} \left( \alpha_n \frac{d\beta_n}{dy} - \beta_n \frac{d\alpha_n}{dx} \right) dy + \frac{\rho}{4\mu} \int_{-b_0}^{b_0} \left( n \frac{d\alpha_n}{dy} - \beta \frac{d\alpha_n}{dx} \right) dy \right]. \tag{77a}
\]

Whence putting \( U + \underline{u} - U \), for \( \underline{u} \) in the left member of equation (77), and integrating by parts, remembering the conditions, this member becomes

\[
\frac{3U_n}{b_0^3} \int_{-b_0}^{b_0} \rho \underline{v}' v' dy + \frac{\rho}{\mu} \int_{-b_0}^{b_0} (u'v')^2 dy \ldots \ldots \ldots \tag{78},
\]

in which the first term corresponds with the first term in the right member of equation (64), which was all that was retained for the criterion, and the second term corresponds with the second term in equation (64), which was neglected.

Since by equation (35)

\[
\frac{3U_n}{b_0^3} = -\frac{1}{\mu \frac{dp}{dx}} \ldots \ldots \ldots \ldots \ldots \tag{78a},
\]

we have, substituting in the discriminating equation (43), either

\[
-\frac{2}{3} \rho \frac{b_0^3}{\mu^2} \frac{dp}{dx} = \frac{2b_0^3}{3} \left( \frac{d}{dy} (\rho W') \frac{dy}{dx} + \frac{\rho^2}{\mu^3} \int_{-b_0}^{b_0} (u'v')^2 dy \right) \ldots \ldots \tag{79},
\]

or

\[
\mu \frac{d^2 \underline{u}}{dy^2} = \frac{dp}{dx} = 0 \ldots \ldots \ldots \ldots \ldots \tag{80}.
\]

Therefore, as long as

\[
-\frac{2}{3} \rho \frac{b_0^3}{\mu^3} \frac{dp}{dx} \leq 2\tag{2}
\]
is of constant value, there is dynamical similarity under geometrically similar circumstances.

The equation (79) shows that,

\[ -\frac{2}{3} \rho \frac{h_0^3}{\mu^2} \frac{d\rho}{dx} \]

is greater than \( K \),

\( \overline{u} \overline{v} \) must be finite, and such that the last term in the numerator limits the rate of transformation, and thus prevents further increase of \( \overline{u} \overline{v} \).

The last term in the numerator of equation (79) is of the order and degree

\[ \rho^3 L^4 \alpha^4 / \mu^3 \] as compared with \( L^4 \alpha^2 \)

the order and degree of \( \frac{1}{\mu} \frac{d}{dt} (\rho \dot{H}) \) the first term in the numerator.

It is thus easy to see how the limit comes in. It is also seen from equation (79) that, above the critical value, the law of resistance is very complex and difficult of interpretation, except in so far as showing that the resistance varies as a power of the velocity higher than the first.
V. On a Method of Determining the Thermal Conductivity of Metals, with Applications to Copper, Silver, Gold, and Platinum.

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Of the different methods hitherto employed for the determination of thermal conductivity of metals, only those which were elaborated by Forbes and by Ångström have been successful in giving absolute results with fair approach to accuracy. The two methods, in the hands of these and subsequent experimenters, have given closely concordant results, both for copper and for iron. They, however, possess the disadvantages of being exceedingly elaborate, requiring, as they do, very extensive preparations and comparatively large masses of the metals which are to be tested. For this reason, only the less costly metals can be tested, as it would be impractically expensive to obtain a bar of gold or platinum, for example, a metre or more in length, and perhaps 2 square centims. section.

The method used in the present investigation (for which a grant of £50 was obtained from the Government Research Fund) is free from these objections. It was suggested by Lord Kelvin as far back as thirty years ago, about the same time that the late Principal Forbes began his experimental inquiry as to whether thermal conductivity varied with temperature. The chief advantages of this method are that (1) it is much simpler than the others; (2) a test of the conductivity of any metal can be made in two or three hours; and (3) (perhaps most important of all) only a few grammes of the metal are necessary. Thus, even the rarest and most expensive metals can be tested, at very moderate cost.

The method is essentially the experimental realization of the theoretical conditions implied in the fundamental formula

$$Q = kA \frac{v - v_0}{l} t$$

where the symbols have their usual meaning. The metals to be tested are made in the form of wires of circular section. One end is kept at a constant temperature $v$, and the flow of heat $Q$, in a given time $t$, is measured. The length and section being known, all the data are obtained for the determination of the absolute value of
the thermal conductivity. It will be noted that this value is the proper mean conductivity corresponding to the range of temperature between the ends of the wire.

Fig. 1 is a perspective drawing of the apparatus which has been used in the tests of this method. Fig. 2 is a section (all the parts being drawn quarter full size) containing the axis of the wire to be tested. Fig. 3 is a section, drawn full size, through the middle of the apparatus, in a plane perpendicular to the section in fig. 2, and showing in greater detail the wire, calorimeter ball, and that part of the heating box at which the wire is soldered.

Referring to fig. 2, W is the wire to be tested. The upper end of W is soldered into the bottom of the copper box B, and the lower end into the solid copper ball C, the diameter of which is 5·5 centims. The sides of the copper box B are of thin sheet copper, and the bottom of copper, 3 millins. thick. B is supported at the middle by being fitted into a rectangular hole in a wooden screen, L, of dimensions 60 × 60 centims., by 2 centims. thick. In the hole of the copper block K, a small thermometer is inserted for measuring the temperature of the other end of the wire. The box B is filled with water and kept boiling briskly. The ball C is the calorimeter by which the amount of heat conducted by the wire W is measured. In order to measure the temperature of C, a very sensitive thermometer, which can be read to one-fortieth of a degree Centigrade, is inserted in a hole drilled in C. This hole reaches to a depth of 3·6 centims. from the circumference of the ball. The bulb of the thermometer in the ball is surrounded by water or mercury. Surrounding
the heating box, B, is an asbestos covering, M, to prevent heat from reaching the calorimeter from the sides of the box. In order to keep the temperature of the air surrounding the calorimeter constant, the latter is surrounded by a water-jacket, R, through which water at the temperature of the air is kept circulating. This water-jacket is simply a cylindrical vessel, made of copper, with double walls, between which the water circulates. The inside diameter is about 1 centim. greater than that of the ball. The top of the water-jacket is covered with three or four layers of paper, so that the air surrounding the ball is completely separated from the outside air, and is kept at a constant temperature. Surrounding the wire, all along its length, is a tube of cardboard, G, of inside diameter 1 centim. Between the wire and the inside of the tube cotton-wool is loosely packed, so as to prevent, as effectually as possible, circulation of air about the wire.

From fig. 2 it will be seen that the heat from the Bunsen is prevented from
reaching the wire or the ball by the wooden screen L. In the bottom of the box, just above the Bunsen, are riveted a number of copper pins, so as to catch and distribute the heat of the burner. Fig. 4 shows a plan of the box.

Fig. 4.

Quarter full size.

It will be convenient to classify the sources of error that may affect the results, and to deal with them at this point.

1. There is, unless proper precautions be taken, loss of heat due to radiation from the surface of the wire, and therefore the value obtained for the conductivity will be too low.

2. The temperature indicated by the thermometer in the hot water may not be the same as that of the end of the wire at the point where it enters the box. Also, the temperature of the ball may not be the same throughout.

3. The thermometer may not indicate the average temperature throughout the ball.

4. There may be a lag in the thermometer.

5. There may be some error due to the solder at the ends of the wire.

1. Loss of heat due to radiation from the surface of the wire. As this was the most obvious source of error, a long time was spent and much work done in investigating it. The cardboard tube G (fig. 2) was found to be thoroughly efficient in preventing radiation. It can be very easily made by rolling a long strip of paper, which has been previously gummed on one side, several times round a circular rod of a centimetre diameter. The length of the tube is a little less than that of the wire. After the gum has dried, a slit sufficiently wide to admit the wire is cut parallel to the length. A circular piece of cardboard is fixed with gum to one end of the tube, as a flange for attaching the tube to the bottom of the heating box. After it has been arranged that the wire is in the central line, cotton-wool is put loosely in and the slit closed up with gummed paper. The small volume of air in this tube takes almost immediately the temperature of the wire all along its length.

To test the efficiency of the tube, a large number of experiments was made, the results of which are given further on (pp. 180, 181). It is clear that for a given difference of temperature between the ends, the loss by radiation from the surface of a wire of given diameter will be greater the greater the length. If, then, there be no error which becomes less the greater the length, and thus compensates for the radiation error, a sufficient test of the efficiency of the tube will be to determine the conductivity with different lengths of the same wire. The shorter lengths ought to give a distinctly higher value, since the radiation from the surface is not only less than in the longer
lengths, but the quantity of heat conducted along the wire per second is greater, and therefore the percentage error due to radiation rapidly diminishes.

In order to determine a superior limit for the error due to loss of heat by radiation, a calculation is made below. The numbers used are taken so as to be as unfavourable as possible, and give a value much higher than what would practically turn out.

In the case of copper wire, the surface was always somewhat tarnished, so the emissivity may be taken as intermediate between those of polished and blackened copper, that is 0.008. The diameter and length of wire were respectively 2 centim. and 4 centims. The temperature at the hot end was 98° C., at the cold end 14° C. The curve of temperature along the wire being logarithmic, the mean temperature will be considerably less than half the sum of the highest and lowest temperatures, which would assume that the curve is a straight line passing through the highest and lowest points. Take, however, the curve to be a straight line; then the mean temperature above that of the air is 42° C. The quantity of heat Q, lost from the surface S, of emissivity E, in one minute, is

\[ Q = ES \times 42 \times 60 \]
\[ = 1.91 \text{ C.G.S. units approximately.} \]

The quantity of heat conducted along the wire during this minute, as taken from one of the tests, was 5 \times 68.9, 5 being the rise in temperature, and 68.9 the capacity of the calorimeter. The maximum percentage error due to radiation in a length of 4 centims. is therefore 5.5 per cent. This is on the assumption that there is no jacket round the wire, but even then the actual loss would probably be less than 3 per cent. if currents of air be avoided. This rough calculation shows that radiation from the surface of the wire need not be considered as an objection to the method.

2. Possible error due to the fact that the thermometers are not actually at the ends of the wire, and so may not be indicating the proper temperatures.

The effect of this error would also be to give too low a value for the conductivity. To guard against this the bottom of the box is made very thick, and the large block K (fig. 2) is added so as to hold the thermometer. The difference of temperature between the inside and outside surfaces of the bottom of the box is certainly exceedingly small, if as much heat as the wire can take away is supplied to it. Since the heat is supplied by boiling water, it is, however, possible that the copper conducts so quickly that there is always a layer of water, it may be thin, immediately in contact with the metal at a very much lower temperature than 100° C. This point is particularly emphasized by Lord Kelvin in volume 3 of his Collected Papers, where he remarks upon the exceedingly low values obtained by Clément and by Péclét for the conductivity of copper. These experimenters both attempted to measure the conductivity by keeping one side of a slab of the metal in contact with water at a constant temperature and measuring the rise in temperature of a known
quantity of water in contact with the other side. The result was that Clément's value was 200 times too small, while Péclet, who tried to avoid Clément's error by having the water violently stirred, succeeded in obtaining a value six times too small. With the large surface to carry away the heat, Péclet's method is useless for any substance having so high a conductivity as even the worst of the metals, since the stirring could never be rapid enough without introducing fresh complications.

The direct tests applied to determine this error in the present investigation showed that the temperatures on the inside and outside of the bottom of the box were the same.

The following approximate calculation serves to show the order of magnitude of the error due to the assumption that the thermometer in the ball indicates the temperature of the end of the wire.

It is clear that the difference of temperatures between the wire where it enters the ball, and the thermometer will be much less than that found as follows:

Take the case of a wire carrying heat to an infinite block of metal whose surface is plane, and remark that the isothermals in the block would be hemispherical surface (fig. 5) having for their common centre the point where the axis of the wire enters the ball, and suppose the flow of heat to be steady.

Let

\[ K = \text{conductivity of the wire}, \]
\[ k = \text{"}, \text{" ball}, \]
\[ a = \text{radius of the wire}, \]
\[ b = \text{"}, \text{" ball}. \]
Then the quantity of heat that flows through any hemispherical surface distant \( r \) from the end of the wire is

\[
Q = -k \frac{dv}{dr} 2\pi r^2;
\]

and, since the flow is steady

\[
\frac{d}{dr} \left( -k \frac{dv}{dr} 2\pi r^2 \right) = 0.
\]

Hence

\[
r^2 \frac{dv}{dr} = C_1,
\]

which gives

\[
v = C_1 r^{-1} + C_2.
\]

For \( r = a \) let \( v = V \), and for \( r = b \) let \( v = \theta \).

Hence

\[
v = ab \frac{V - \theta}{b - a} r^{-1} + \frac{\theta b - Va}{b - a},
\]

whence

\[
- \frac{dv}{dr} = ab \frac{V - \theta}{b - a} r^{-3};
\]

and

\[
Q = 2\pi k \frac{V - \theta}{b - a} ab.
\]

Also

\[
Q = (V_1 - V) \frac{\pi a^2 K}{l}
\]

where \( V_1 \) is the temperature at the hot end of the wire, and \( l \) the length of the wire.

Since \( V \) is the temperature of the wire just where it enters the ball, and \( \theta \) the temperature at the centre of the ball, \( V - \theta \) is certainly much greater than the error, a superior limit to the magnitude of which we wish to ascertain. The heat which flows through the wire must be equal to that which flows into the ball; therefore

\[
(V_1 - V) \frac{\pi a^2 K}{l} = 2\pi k \frac{V - \theta}{b - a} ab,
\]

whence

\[
V - \theta = (V_1 - V) \frac{a}{2l} \frac{K}{k} \frac{(b - a)}{b}
\]

\[
= - (V - \theta + \theta - V_1) \frac{a}{2l} \frac{K}{k} \frac{(b - a)}{b},
\]

and, therefore,

\[
V - \theta = (V_1 - \theta) \frac{\frac{a}{2l} \frac{K}{k} \frac{(b - a)}{b}}{1 + \frac{a}{2l} \frac{K}{k} \frac{(b - a)}{b}}.
\]
MR. J. H. GRAY ON A METHOD OF DETERMINING

In this case $V_1 = 100^\circ C$, $\theta = 15^\circ C$, and, since the copper of the wire and ball were the same, $K/k = 1$; $b = 27$ millims., $a = 1$ millim.

Take $l = 8$ centims.; then,

$$V - \theta = 85\left(\frac{\frac{1}{\pi} \frac{2\theta}{2\theta}}{1 + \frac{1}{60} \frac{2\theta}{2\theta}}\right) = 5^\circ C.$$

Take $l = 3$ centims., which is less than the shortest length used;

then

$$V - \theta = 85\left(\frac{\frac{1}{\pi} \frac{2\theta}{2\theta}}{1 + \frac{1}{60} \frac{2\theta}{2\theta}}\right) = 1\cdot3^\circ C.$$

Therefore $1\cdot3^\circ C.$ is greater than the extreme possible error made with the copper wire, that is $1\cdot3$ in $85$, or about $1\cdot5$ per cent.

Several attempts were made to obtain a direct test of this by applying a thermo-electric junction to the wire just at the point where it entered the ball. Owing, however, to the large mass of the ball which had to be heated, it was found most difficult to solder the thin wires of the thermo-electric junction at the required place, and, after several unsuccessful attempts, it was given up, as the indirect proof supplied by using different lengths of wire seemed quite satisfactory.

3. The thermometer in the ball may not indicate the average temperature.

This also would be tested by using different lengths of wire, and, as will be seen, the results show that there was no substantial variation.

4. Lag in the thermometer which measures the rise in temperature of the ball. Here again different lengths will be a test. Also, in case that the water round the bulb of the thermometer caused the lag, mercury was substituted, but no difference in the result was obtained.

5. The solder at the ends did not cause any difference of value for different lengths.

The method of conducting a test is as follows.

Take a length of not more than 8 centims. of the wire. As it is very easy to obtain any diameter, it will be convenient to have a hole bored in the bottom of the heating box, just below the thermometer, of diameter rather more than 2 millims., and depth 3 or 4 millims. The heating box must be brazed together, otherwise it is apt to fall to pieces when the wire is being soldered in. The latter process can be done with ordinary solder.

The mass of copper in the box being considerable, it is rather a troublesome matter to solder the wire into it, as the whole box has to be heated. For this reason a soldering iron cannot be used. The box is most easily heated by a blow-pipe flame and the wire then inserted. The extra solder is then cleared off, so as to give a definite point from which to measure the length. After this end is fixed, the other end is soldered in a similar manner to the copper ball, and in the latter case fusible solder melting at about $100^\circ C.$ will do quite well.
The Thermal Conductivity of Metals

It was, however, found that the method of soldering just described, and used in this investigation, was very troublesome, and required some practice. If new apparatus were being made, it would certainly be much more convenient to make an alteration in this respect.

The following plan would make the soldering of the wire a very easy process, instead of, as described, a difficult one. Six copper plugs, each of the shape shown in sectional elevation and plan in fig. 6, might be made, 8 millims. in length, and 1 centim. diameter, so as to screw into a corresponding hole in the bottom of the heating box; and six similar plugs might be made for the ball. In each of the plugs the central hole might be made of a different diameter, varying from 2 to 4 millims. In this way, wires of different diameters could very easily be soldered into the suitable plugs, which could then be screwed, first the one end into the ball, then the other end into the box. The two side holes shown in fig. 6 are for the purpose of facilitating the screwing in of the plugs. By screwing into the ball first, the possibility of twisting the wire is avoided. It is advisable not to use wire of diameter much less than 2 millims., for, in wires of less diameter, the length required to give a readable rise of temperature per minute becomes inconveniently small, unless the calorimeter ball is made very small.

The calorimeter ball most frequently used in the present work was turned from the solid, and is 5·5 centims. in diameter. This was found to be a very convenient size for the metals of high conductivity—for example, gold, silver, and copper. Any length from 4 to 8 centims. of wires of these metals may be used without making it difficult to read the rise in temperature per minute. It is not advisable to use lengths shorter than 4 centims., as there is then a danger of the water-jacket being too near the heating-box, but it is better to use a smaller ball, say of 4 centims. diameter, for metals of lower conductivity. For metals having conductivities between 1·0 and 0·7 C.G.S. units, the large ball was found to be quite convenient; for lower values the smaller ball was used. The object aimed at was to arrange the dimensions so as to enable an experiment to be finished in less than half an hour from the time that one end was made hot by the boiling water.

After the wire has been soldered in, the box is placed in the screen L (fig. 2), and fixed by any convenient means, so that the wire hangs vertical, and the asbestos cover is put over the box. The cardboard tube, having been made of suitable length, and slit along its length, is now slipped round the wire, and, after a little cotton is loosely packed in, the slit is closed up by means of a strip of gummed paper.
The wire is now completely enclosed in this tube, and loosely surrounded by cotton wool.

The thermometer is placed in the hole in the ball, and a little water put in to fill up the hole. The water-jacket may then be raised so as to surround the ball, and the top of the water-jacket must be covered with two or three sheets of paper, holes having been cut in these, so as to admit the wire and thermometer.

It was found best to make these preparations a few hours before the actual test was begun, so as to allow the system to take up a permanent temperature. When it has been ascertained that this temperature has been reached, a reading is taken from the thermometer in the ball. The thermometer used was most carefully made and calibrated for the tests by Mr. Otto Müller, of Glasgow. The whole length of the stem is 15 centims., and it is marked off to read twentieths of a degree from 9° to 20° C. Each division is a half millimetre, so it is perfectly easy to read to one-fourtieth of one degree.

Before beginning the test, the water-jacket is lowered, and a vessel containing ice and water raised so as to cover a part of the ball. By this means the temperature of the ball is lowered by 6° or 7° below that of the air. While this is being done, the boiling water is poured into the box, so as to nearly fill it, and the Bunsen lamp lit. The water soon begins to boil rapidly, and the thermometer (which is 12 centims. long and reads from 95° to 105° C.) indicates a constant temperature, usually 97° or 98° C. When the temperature of the ball has been lowered 6° or 7°, the ice and water are taken away, and the ball is carefully dried with a soft cloth. The water-jacket is again placed so as to surround the ball and the cover put on as before, the circulation of water in the jacket having been started.

It is now only necessary to take readings of both thermometers every half minute. The temperature of the hot water will be practically constant, but it is advisable to take the readings in case of alteration. The calorimeter thermometer may be read till it reaches 20° C.

It will be convenient to explain here the reason for cooling the ball 6° or 7° before starting. In the preceding remarks no notice was taken of the fact that there will be radiation to or from the surface of the ball unless the latter is at the same temperature as its surroundings. It would be impossible to allow for this by calculation, as the surface is altered before every test by being heated while the wire is being soldered into the ball. For the purpose of getting rid of the necessity of allowing for this radiation, the ball is cooled down.

Let $Q_1 =$ the quantity of heat which flows along the wire in unit time when the hot end is at $T°$ and the cool end at $\theta°$ above the temperature $t$ of the air and water-jacket, and let $Q_2 =$ the quantity when the cool end is $\theta°$ below that of the air.

Then, assuming that the conductivity does not change very much through $2\theta°$, and that $\alpha$, the loss by radiation in unit time when the ball is $\theta°$ above the air tempera-
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ture, is equal to the gain by absorption in unit time when the ball is \( \theta \) below the air temperature, we have

\[
Q_1 = \frac{KA}{l} [T - (t + \theta)] - a
\]

and

\[
Q_2 = \frac{KA}{l} [T - (t - \theta)] + a.
\]

Therefore

\[
\frac{Q_1 + Q_2}{2} = \frac{KA}{l} (T - t).
\]

It is seen by the last equation that the effect of radiation to or from the surface of the ball is completely eliminated since the coefficient of emission is numerically equal to the coefficient of absorption for the same difference of temperatures. It therefore fortunately does not matter how the surface of the ball becomes changed, so long as it remains the same during the half hour of the experiment. As a matter of fact, during the soldering process the surface becomes very much tarnished.

Table I gives a specimen experiment taken at random from my laboratory book.

**Friday, 23rd March, 1894.**—Pure Silver Wire (annealed). Length = 6'59 centims. Diameter = 0'202 centim. Temperature of Air = 14'3° C.

<table>
<thead>
<tr>
<th>1. Reading taken every half-minute.</th>
<th>II. Temperature of hot end.</th>
<th>1. Reading taken every half-minute.</th>
<th>II. Temperature of hot end.</th>
</tr>
</thead>
<tbody>
<tr>
<td>° C.</td>
<td>° C.</td>
<td>° C.</td>
<td>° C.</td>
</tr>
<tr>
<td>10'3</td>
<td>98'2</td>
<td>14'75</td>
<td>98'3</td>
</tr>
<tr>
<td>10'5</td>
<td>98'2</td>
<td>14'9</td>
<td>98'4</td>
</tr>
<tr>
<td>10'75</td>
<td>98'2</td>
<td>15'1</td>
<td>98'6</td>
</tr>
<tr>
<td>10'95</td>
<td>98'3</td>
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<td>98'6</td>
</tr>
<tr>
<td>11'35</td>
<td>98'2</td>
<td>15'6</td>
<td>98'4</td>
</tr>
<tr>
<td>11'55</td>
<td>98'3</td>
<td>15'75</td>
<td>98'4</td>
</tr>
<tr>
<td>11'75</td>
<td>98'3</td>
<td>15'9</td>
<td>98'6</td>
</tr>
<tr>
<td>11'95</td>
<td>98'2</td>
<td>16'05</td>
<td>98'5</td>
</tr>
<tr>
<td>12'15</td>
<td>98'3</td>
<td>16'25</td>
<td>98'6</td>
</tr>
<tr>
<td>12'35</td>
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<td>16'4</td>
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</tr>
<tr>
<td>12'55</td>
<td>98'3</td>
<td>16'55</td>
<td>98'6</td>
</tr>
<tr>
<td>12'75</td>
<td>98'5</td>
<td>16'7</td>
<td>98'6</td>
</tr>
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</tr>
<tr>
<td>13'1</td>
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<td>17'0</td>
<td>98'6</td>
</tr>
<tr>
<td>13'3</td>
<td>98'3</td>
<td>17'15</td>
<td>98'6</td>
</tr>
<tr>
<td>13'5</td>
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<tr>
<td>13'75</td>
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<td>98'6</td>
</tr>
<tr>
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<td>17'6</td>
<td>98'6</td>
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<tr>
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<td>17'7</td>
<td>98'7</td>
</tr>
<tr>
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<td>17'86</td>
<td>98'6</td>
</tr>
<tr>
<td>14'4</td>
<td>98'4</td>
<td>18'0</td>
<td>98'6</td>
</tr>
<tr>
<td>14'6</td>
<td>98'3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The numbers in column 1. are put on a curve, as shown in diagram II. From this curve the rise in temperature in half a minute is read off for \( x^\prime \) above the temperature of the air, and this is added to the rise for \( x^\prime \) below the temperature of the air, where \( x \) is any value from 0 to 5 or 6. In this way as many as 10 or 15 values are obtained. If the curve were quite regular, each of these values would be the same, since they each represent the rise in temperature per minute for the same difference of temperature, but they are found to vary by about 1 or 2 per cent. But, by taking the mean of 10 or 15 values, it will be seen that the result obtained must be very near the correct value for the rise between the given temperatures. It is then only necessary to multiply this rise in temperature by the thermal capacity, \( C \), of the ball to find the quantity of heat that has passed along the wire in one minute, and the conductivity can be calculated from the formula

\[
K = \frac{C\theta l}{\pi r^2 (T - t) 60}
\]

where \( r \) is the radius of the wire.

In order to obtain an accurate determination of the thermal capacity of the ball, I took it to Dublin, where the capacity was most carefully determined for me, during the time I was there, by Dr. John Joly, F.R.S., by his most ingenious steam calorimeter method.\(^*\) I have to thank Dr. Joly for the trouble to which he put himself in making the determination.

As the most important thing in testing the method is to show that with different lengths the resulting determination of the conductivity remains practically the same, these series of tests and the results will be given first.

The wire first used was what was called six years ago high electrical conductivity copper. The diameter was 2·1 millims., density 8·85, volume specific (electrical) resistance, 1834 in electromagnetic units. This wire was almost exclusively used, but in the course of the work tests were made of wire got from Messrs. Glover and Co. in the end of the year 1890. Messrs. Glover's wire was found to have considerably higher conductivity, both electrically and thermally, than the first-mentioned wire, which for convenience will be called the laboratory copper, as it was what was used for all the electrical work in the laboratory. Taking the laboratory wire as 100 per cent. conductivity (thermally and electrically), it was found that Messrs. Glover's wire was 106·6 per cent. electrical, and 108 per cent. thermal conductivity.

These results will be referred to further on (p. 180). They are merely mentioned here to show that the best conducting wire was not used for the exhaustive tests.

Table II. shows the record of series of experiments made on laboratory copper wire. The wire was soldered into the heating box and ball as described; an experiment was made and the length measured carefully. The ball was then heated by a blow-

pipe flame to allow the wire to be taken out. A short piece was then cut off and the shortened wire again soldered into the ball.

Table II.—Showing rise of Temperature of Calorimeter Ball with time.
Diameter of wire = 210 centim. Temperature readings taken every half-minute.

<table>
<thead>
<tr>
<th>Length = 6'31 centims.</th>
<th>Length = 5'87 centims.</th>
<th>Length = 5'23 C.</th>
<th>Length = 4'33 centims.</th>
<th>Length = 4'01 centims.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. reading at every half-minute.</td>
<td>Temp. reading at every half-minute.</td>
<td>Temp. reading at every half-minute.</td>
<td>Temp. reading at every half-minute.</td>
<td>Temp. reading at every half-minute.</td>
</tr>
<tr>
<td>°C.</td>
<td>°C.</td>
<td>°C.</td>
<td>°C.</td>
<td></td>
</tr>
<tr>
<td>6-45</td>
<td>6-25</td>
<td>7-0</td>
<td>6-55</td>
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<td>6-65</td>
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<td>6-85</td>
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<td>7-05</td>
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<td>9-2</td>
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<td>9-4</td>
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<td>11-8</td>
<td>12-0</td>
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<td>11-95</td>
<td>12-15</td>
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<td>14-0</td>
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<td>12-35</td>
<td>14-25</td>
<td>15-1</td>
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<td>12-25</td>
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<td>13-05</td>
<td>16-8</td>
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</tr>
</tbody>
</table>

Temp. of air 9° 85 C. | Temp. of air 9° 1 C. | Temp. of air 10° 0 C. | Temp. of air 10° 35 C. | Temp. of air 12° 3 C. |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. of hot water 97° 3 C.</td>
<td>Temp. of hot water 97° 0 C.</td>
<td>Temp. of hot water 97° 0 C.</td>
<td>Temp. of hot water 96° 4 C.</td>
<td>Temp. of hot water 96° 7 C.</td>
</tr>
</tbody>
</table>

MDCCCLXCV.—A. 2 A
The temperature of the hot water varied not more than half a degree during an experiment, and the value given in each column of the preceding Table is the mean throughout the time. The columns of temperatures were, immediately after an experiment, put on a curve with time as abscissæ. The effect of radiation to and from the calorimeter ball is fairly well marked. At the point corresponding to the temperature of the air in each curve there is an increase of curvature, caused by the fact that the radiation has changed from negative to positive.

In order to find the flow of heat, the rise of temperature per minute was read from the curve at a temperature \( x^\circ \) below that of the air, and this was added to the rise for \( x^\circ \) above that of the air. \( x \) varied from 0° to 4° or 5°. By this means from ten to fifteen readings were got, and the mean of these gave the rise at the temperature of the air.

For example, for the length 6·31 centims. in the first column of Table I., the rise thus obtained from the curve, Diagram I., was 3605 in one minute. The capacity of the ball and of the part of the thermometer with the water in the hole was found to be 68·9.

There

\[
K = \frac{68.9 \times 3605 \times 6.31}{\pi \times (1.05)^2 \times 87.45 \times 60}
\]

\[= 883 \text{ C.G.S. unit.}\]

This value is not corrected for the error given by the approximate formula already mentioned.

Error

\[
=(V_1 - \theta) \left( \frac{a}{2l} \frac{K}{b} \frac{b - a}{b} \right)
\]

\[= (\theta - \theta) \left( \frac{a}{2l} \frac{K}{b} \frac{b - a}{b} \right)
\]

\[= -0.69^\circ \text{ in this case.}\]

This makes the difference of temperature less by \( 0.7^\circ \), and when this correction is made we get for the conductivity 889 C.G.S. unit. The conductivity as calculated from five different lengths becomes, after the correction is made—

<table>
<thead>
<tr>
<th>Length in centims.</th>
<th>Conductivity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.31</td>
<td>889</td>
</tr>
<tr>
<td>5.87</td>
<td>893</td>
</tr>
<tr>
<td>5.23</td>
<td>890</td>
</tr>
<tr>
<td>4.99</td>
<td>887</td>
</tr>
<tr>
<td>4.015</td>
<td>883</td>
</tr>
</tbody>
</table>

The greatest difference between these values is a little over 1 per cent. Taking
their mean, we get for the thermal conductivity of the laboratory copper wire \(0.8884\) C.G.S. unit. This value is the mean conductivity between the temperatures 97° C. and 10° C.

The following Table gives the results of a series of tests on another portion of the same wire:

<table>
<thead>
<tr>
<th>Length in centims.</th>
<th>Conductivity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.11</td>
<td>0.888</td>
</tr>
<tr>
<td>5.71</td>
<td>0.883</td>
</tr>
<tr>
<td>4.80</td>
<td>0.892</td>
</tr>
<tr>
<td>4.43</td>
<td>0.889</td>
</tr>
</tbody>
</table>

The mean of these values is 0.8880, being \(\frac{1}{23}\) per cent. less than that obtained from the preceding series.

Taking Ångström’s formula,

\[
K = 1.027 (1 - 0.00214t),
\]

and finding \(K\) for 53°, which is the mean of 97° and 10°, we get \(K = 0.9203\) C.G.S. unit.

The close agreement in the values obtained with different lengths shows that the errors already mentioned as possible are practically eliminated. Ångström’s value is 4.5 per cent. greater than 0.8884, but, as has been mentioned (p. 176), the conductivity of the laboratory copper wire is 8 per cent. less than that of Glover’s wire afterwards tested. In a previous paper, Ångström gives 0.91 as the value for 51.3° C.

In a paper read before the Royal Society last year, Dr. R. W. Stewart, using the Forbes method, but substituting a single thermo-electric junction for the thermometers, gives the values for copper and iron. At the temperature 53° C. he gets for copper \(K = 1.067\), which is 10 per cent. higher than the value obtained for any specimen of copper tested in the present investigation.

The conductivity of the wire obtained from Messrs. Glover and Son was found to be 0.9594 C.G.S. This was the best conducting copper tested by the present method. The specific electrical resistance was 1730 in absolute units.

To test separately the effect of any alterations, separate experiments were made.

I. Instead of enclosing the whole length of the wire (laboratory copper) in a tube, only a part was enclosed.

The paper tube was shortened by 2 or 3 millims. each time, and the conductivity of the same length of wire was determined after each shortening of the tube. The result found was, that the shortening (which was, of course, done from the cool end of the wire) had practically no effect on the value so long as it was arranged that there were no draughts of cold air. If for no other reason, the paper tube is necessary to
prevent draughts, as the latter make a determination impossible. It was found that
the paper tube could be shortened as much as to leave the lower half of the wire
exposed without any appreciable diminution of the value obtained. When it was
shortened much further, the value began to diminish till, when the tube was removed
altogether, the value obtained was found to be fully 6 per cent. lower than when the
tube completely covered the wire. When the wire was bare it was found very
difficult to prevent draughts caused by the hot wire, and these draughts made the
readings of the thermometer very irregular.

In connection with this, it will be noted that there is a particular advantage
in having the calorimeter ball lower in position than the heating box, as the hot air
round the latter rises, and so does not affect the water-jacket. It has been suggested,
however, that a separate experiment should be made to test whether any heat reached
the ball otherwise than through the wire. For this purpose the ball was suspended
by silk threads, in such a way that its highest point was 4·4 centimetres from the
bottom of the heating box. The water jacket was placed round the ball, and the
sheets of paper put on the top of the jacket. The water in the heating box was kept
boiling for twenty-five minutes, and the temperature of the ball, as indicated by the
thermometer in it, was noted at intervals. No change in the thermometer reading
could be detected, although \( \frac{1}{40} \) th of one degree can be read without difficulty on the
thermometer scale.

As a further test of the effect of the paper tube, the upper half length of the wire
which was being tested, was left unprotected by any tube, while the lower half was
enclosed. The result was practically the same as if there had been no tube at all.

In order to make certain that the thermometer in the hot water indicated the
temperature of the upper end of the wire, a thermo-electric junction was used. The
junction was made of very thin wires of copper and platinoid, and, after being wrapped
once round the hot end of the wire just at the end, was soldered there. The other
junction was fixed to a thermometer and immersed in water. The heating box was
then filled with water, which was kept boiling. The water in the vessel containing
the other junction was gradually heated up till there was no deflection in the mirror
galvanometer used. Both junctions must then be at the same temperature. When
there was no deflection in the galvanometer the thermometers were found to be
indicating the same temperatures.

Several qualities of copper were tested, the results of which are given below.

Copper wire, made by Messrs. Bolton and Co., Cheadle. This wire was by
mistake sent away before its electrical conductivity was measured, and it cannot be
got again.
The greatest variation here is 1 per cent., and the mean value is \( \text{0.8612} \).

Some specimens of copper wire were bought in a plumber's shop, of quality used for bell-hanging.

<table>
<thead>
<tr>
<th>Specimen.</th>
<th>Diameter (in centims.)</th>
<th>Specific resistance (electrical)</th>
<th>Mean thermal conductivity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-200</td>
<td>5545</td>
<td>-3198</td>
</tr>
<tr>
<td>2</td>
<td>-204</td>
<td>4701</td>
<td>-3497</td>
</tr>
</tbody>
</table>

\[
\frac{\text{Conductivity of Laboratory wire}}{\text{Conductivity of Specimen 1}} = 2.78 \quad \text{for heat,}
\]
\[
= 2.86 \quad \text{for electricity.}
\]
\[
\frac{\text{Conductivity of Laboratory wire}}{\text{Conductivity of Specimen 2}} = 2.54 \quad \text{for heat,}
\]
\[
= 2.56 \quad \text{for electricity.}
\]
\[
\frac{\text{Conductivity of Glover's wire}}{\text{Conductivity of Laboratory wire}} = 1.08 \quad \text{for heat,}
\]
\[
= 1.066 \quad \text{for electricity.}
\]

In all the wires tested it was found that if one metal was a better conductor for electricity it was also better for heat. This has been noticed by several investigators, notably Professor Tait, and Wiedemann and Franz. Beyond this the present results cannot go, as enough trials were not made to allow of comparison. Previous experimenters have found that the ratio of electrical conductivities of two wires is not exactly equal to the ratio of thermal conductivities. This is indeed to be expected, if the coefficients already obtained for the alteration with temperature are accurate. For example, in copper the coefficient of variation per degree for electrical conductivity is very much greater than that found for thermal conductivity, so that, even if the ratios were equal at one temperature, they must be unequal at all other temperatures. In some of the wires tested the electrical and thermal ratios differed by as much as 4 or 5 per cent.

Before the present investigation, the absolute values for the conductivity of the
more expensive metals had not been determined, although relative values had been found by Wiedemann and Franz.*

I am very much indebted to Messrs. Johnson, Matthey, and Co. for their great kindness in preparing and lending to me wires of gold, platinum, silver, and other pure metals, of 2 millims. diameter, and of such a length as to enable me to measure without difficulty both the thermal and electrical conductivities.

Unfortunately, I cannot find a record of the value obtained for the electrical conductivity of the gold wire, and it has been returned some time ago. As, however, Messrs. Johnson, Matthey, and Co. stated, when sending it, that it was as pure as could be made, it will perhaps be sufficient for me to use the value that has already been found for the electrical conductivity of gold as determined by other experimenters.

The curves for the calculation of the conductivity of silver wire are shown in Diagram II. The values for the different lengths are given below.

**Silver Wire.**

<table>
<thead>
<tr>
<th>Length</th>
<th>Thermal conductivity in C.G.S. units between 15° C. and 98° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7\text{.}86</td>
<td>0\text{.}956</td>
</tr>
<tr>
<td>6\text{.}59</td>
<td>0\text{.}960</td>
</tr>
<tr>
<td>6\text{.}59</td>
<td>0\text{.}963</td>
</tr>
<tr>
<td>5\text{.}61</td>
<td>0\text{.}973</td>
</tr>
</tbody>
</table>

It will be observed that the second and third values, although for the same length, differ by about \(\frac{1}{2}\) per cent. They are both given however, as they agree within the limits of observational errors. The mean of these values is 0\text{.}9628.

As the curves for gold and platinum are very similar to those for copper and silver, it may be enough to give the values obtained for their conductivities.

**Gold Wire (not annealed).** Diameter = 0\text{.}202 centim.

<table>
<thead>
<tr>
<th>Thermal conductivity in C.G.S. unit.</th>
<th>Electrical resistance as determined by Dr. Matthiessen.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0\text{.}7464</td>
<td>2188</td>
</tr>
</tbody>
</table>

Comparing these values with those for Messrs. Glover's copper, which was found to be 0\text{.}959, we find that the thermal conductivity of gold is 78 per cent. and the electrical conductivity 81\text{.}6 per cent. that of copper.

* 'Annales de Chemie,' vol. 41, p. 107, 1854.
THE THERMAL CONDUCTIVITY OF METALS.

Platinum Wire (not annealed). Diameter = 202 centim.

<table>
<thead>
<tr>
<th>Thermal conductivity.</th>
<th>Electrical resistance.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1861</td>
<td>9180</td>
</tr>
</tbody>
</table>

Here the thermal and electrical conductivities are each 19 per cent. of the conductivity of copper.

The gold, platinum, and silver were afterwards carefully annealed by Messrs. Johnson, Matthey, and Co., and the conductivities again determined. In each of the cases the alteration due to annealing was less than 1 per cent. both in electrical and thermal conductivity.

The results for the different metals are therefore—

**Mean Conductivity between Temperatures 10° C. and 97° C.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Conductivity</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>9594</td>
<td>2·00</td>
</tr>
<tr>
<td></td>
<td>8884</td>
<td>2·11</td>
</tr>
<tr>
<td></td>
<td>8612</td>
<td>3·09</td>
</tr>
<tr>
<td>Very impure</td>
<td>3·497</td>
<td>2·04</td>
</tr>
<tr>
<td></td>
<td>3·193</td>
<td>2·04</td>
</tr>
<tr>
<td>Silver</td>
<td>9628</td>
<td>2·02</td>
</tr>
<tr>
<td>Gold</td>
<td>7464</td>
<td>2·00</td>
</tr>
<tr>
<td>Platinum</td>
<td>1861</td>
<td>2·00</td>
</tr>
</tbody>
</table>

It is intended to use other liquids than boiling water to heat one end of the wire, and in this way test the alteration of conductivity with temperature. Up to the present time no alloys have been tested, but it is intended that tests should be made of some, such as platinoid and German silver; also iron, as pure as possible, might be tested.

Instead of boiling water, steam was used for some time in this investigation, and was in some respects found to be more convenient. Fig. 7 is a sketch showing a section through the middle of the apparatus.

The steam is generated in the vessel W, passes along the upper tube T in the direction of the arrows, and blows directly on the end of the wire, afterwards passing out through the outside copper tube P, and escaping by the outlet B.

The thermometer D indicates the temperature of the steam just when it strikes the wire. It will be seen that the outer tube with the steam in it serves as a steam jacket, and thus keeps the steam in the inner tube T at a high temperature. The sloping bottom where the wire is fixed at A is so made to prevent water accumulating there. To ensure that as much steam as will supply all the heat that the copper can take up is impinging at A, it is only necessary to arrange that the steam emerges at B as steam.

MDCCCXCV.—A.
The outside tube need not be more than 4 centims. diameter, and may be round, but the part where the wire is soldered in must be thickened and made as shown in the sketch, so that there may be no risk of water gathering above the wire. The length of the tube need not exceed 15 centims. This allows sufficient length for the tube to be inserted into the screen, which prevents the heat of the lamp from altering the temperature of the ball. The diameter of the inside tube may be 1.5 centims. With this apparatus most satisfactory results were obtained.

When a metal is tested for the first time, it will be advisable to find its approximate thermal conductivity by comparing its electrical conductivity with copper. This will give an idea as to which calorimeter ball to use, and what length of wire will give a convenient rise of temperature per minute. A test is then almost as simple as for electrical conductivity.
VI. Argon, a New Constituent of the Atmosphere.

By Lord Rayleigh, Sec. R.S., and Professor William Ramsay, F.R.S.

Received and Read January 31, 1895.

"Modern discoveries have not been made by large collections of facts, with subsequent discussion, separation, and resulting deduction of a truth thus rendered perceptible. A few facts have suggested an hypothesis, which means a supposition, proper to explain them. The necessary results of this supposition are worked out, and then, and not till then, other facts are examined to see if their ulterior results are found in Nature."—De Morgan, "A Budget of Paradoxes," ed. 1872, p. 55.

1. Density of Nitrogen from Various Sources.

In a former paper* it has been shown that nitrogen extracted from chemical compounds is about one-half per cent. lighter than "atmospheric nitrogen."

The mean numbers for the weights of gas contained in the globe used were as follows:

- From nitric oxide . . . . 2.3001
- From nitrous oxide . . . . 2.2990
- From ammonium nitrite . . . . 2.2987

while for "atmospheric" nitrogen there was found—

- By hot copper, 1892 . . . . 2.3103
- By hot iron, 1893 . . . . 2.3100
- By ferrous hydrate, 1894 . . . . 2.3102

At the suggestion of Professor Thorpe, experiments were subsequently tried with nitrogen liberated from urea by the action of sodium hypobromite. The carbon and hydrogen of the urea are supposed to be oxidized by the reaction to CO₂ and H₂O, the former of which would be retained by the large excess of alkali employed. It was accordingly hoped that the gas would require no further purification than drying. If it proved to be light, it would at any rate be free from the suspicion of containing hydrogen.

The hypobromite was prepared from commercial materials in the proportions recommended for the analysis of urea—100 grams. caustic soda, 250 cub. centims. water, and 25 cub. centims. of bromine. For our purpose about one and a half times the above quantities were required. The gas was liberated in a bottle of about 900 cub. centims. capacity, in which a vacuum was first established. The full quantity of hypobromite solution was allowed to run in slowly, so that any dissolved gas might be at once disengaged. The urea was then fed in, at first in a dilute condition, but, as the pressure rose, in a 10 per cent. solution. The washing out of the apparatus, being effected with gas in a highly rarefied state, made but a slight demand upon the materials. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment, the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The “inert and inodorous” gas attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were in great degree obviated by passing the gas over hot metals. For the fillings of June 6, 9, 13, the gas passed through a short length of tube containing copper in the form of fine wire, heated by a flat Bunsen burner, then through the furnace over red-hot iron, and back over copper oxide. On June 19 the furnace tubes were omitted, the gas being treated with the red-hot copper only. The results, reduced so as to correspond with those above quoted, were—

<table>
<thead>
<tr>
<th>June</th>
<th></th>
<th></th>
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</thead>
<tbody>
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<td></td>
<td>6</td>
<td>9</td>
<td>13</td>
<td>19</td>
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<td>2.2978</td>
<td>2.2987</td>
<td>2.2982</td>
<td>2.2994</td>
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Without using heat it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed, and air simply bubbled through the hypobromite solution is allowed to pass with constant shaking over mercury contained in a U tube, the surface of the metal was soon fouled. When hypochlorite was substituted for hypobromite in the last experiment there was a decided improvement, and it was thought desirable to try whether the gas prepared from hypochlorite and urea would be pure on simple desiccation. A filling on June 25 gave as the weight 2.3343, showing an excess of 36 mgs., as compared with other chemical nitrogen, and of about 25 mgs. as compared with atmospheric nitrogen. A test with alkaline pyrogallate appeared to prove the absence from this gas of free oxygen, and only a trace of carbon could be detected when a considerable quantity of the gas was passed over red-hot cupric oxide into solution of baryta.
Although the results relating to urea nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes, whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The solution of potassium nitrite and ammonium chloride was heated in a water-bath, of which the temperature rose to the boiling-point only towards the close of operations. In the earlier stages the temperature required careful watching in order to prevent the decomposition taking place too rapidly. The gas was washed with sulphuric acid, and after passing a Nessler test, was finally treated with potash and phosphoric anhydride in the usual way. The following results have been obtained:

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<tr>
<td></td>
<td>4</td>
<td>2·2983</td>
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<tr>
<td></td>
<td>9</td>
<td>2·2989</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>2·2990</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>2·2987</td>
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It will be seen that in spite of the slight nitrous smell there is no appreciable difference in the densities of gas prepared from ammonium nitrite with and without the treatment by hot metals. The result is interesting, as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus:

- From nitric oxide: 2·3001
- From nitrous oxide: 2·2990
- From ammonium nitrite purified at a red heat: 2·2987
- From urea: 2·2985
- From ammonium nitrite purified in the cold: 2·2987

Mean: 2·2990

These numbers, as well as those above quoted for "atmospheric nitrogen," are subject to a correction (additive)* of `0006 for the shrinkage of the globe when exhausted.† If they are then multiplied in the ratio of 2·3108:1·2572, they will express the weights of the gas in grams per litre. Thus, as regards the mean numbers, we find as the weight per litre under standard conditions of chemical nitrogen 1·2511, that of atmospheric nitrogen being 1·2572.

[* In the Abstract of this paper (Proc. Roy. Soc., vol. 57, p. 265) the correction of `0006 was erroneously treated as a deduction.—April, 1885.]
It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have \( \text{N}_2 : \text{O}_3 = 2:2996 : 2:6276 = 0:87517 \); so that if \( \text{O}_2 = 16 \), \( \text{N}_2 = 14:008 \). Thus, when the comparison is with chemical nitrogen, the ratio is very nearly that of 16 : 14. But if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

The determination by Stas of the atomic weight of nitrogen from synthesis of silver nitrate is probably the most trustworthy, inasmuch as the atomic weight of silver was determined with reference to oxygen with the greatest care, and oxygen is assumed to have the atomic weight 16. If, as found by Stas, Ag NO\(_3\) : Ag = 1:57490 : 1, and Ag : O = 107:930 : 16, then N : O = 14:049 : 16.

To the above list may be added nitrogen, prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride, and afterwards liberated in the free state by means of calcium hypochlorite. The purification was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:

\[
\begin{align*}
\text{Globe empty, October 30, November 5} & \quad 2'82313 \\
\text{Globe full, October 31} & \quad 52395 \\
\text{Weight of gas} & \quad 2'29918
\end{align*}
\]

It differs inappreciably from the mean of other results, viz., 2'2990, and is of special interest as relating to gas which, at one stage of its history, formed part of the atmosphere.

Another determination with a different apparatus of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated to dryness; the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly prepared solution of sodium hypobromite. The nitrogen was collected in a gas-holder over water which had previously been boiled, so as at all events partially to expel air. The nitrogen passed into the vacuous globe through a solution of potassium hydroxide, and through two drying-tubes, one containing soda-lime, and the other phosphoric anhydride.

At 18°38' C. and 754'4 mgs. pressure, 162'843 cub. centims. of this nitrogen weighed 0'18963 gram. Hence:

\[
\text{Weight of 1 litre at 0° C. and 760 millims. pressure} \quad 1'2521 \text{ gram.}
\]
The mean result of the weight of 1 litre of "chemical" nitrogen has been found to equal 1.2511. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia, produced from the magnesium nitride, is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose, the ammonia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardized by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 cubic centim. precipitated the chlorine from 0.001701 gram. of ammonium chloride.

1. Ammonium chloride from orange-coloured sample of magnesium nitride.
   0.1106 gram. required 43.10 cub. centims. of silver nitrate = 66.35 per cent. of chlorine.

2. Ammonium chloride from blackish magnesium nitride.
   0.1118 gram. required 43.6 cub. centims. of silver nitrate = 66.35 per cent. of chlorine.

3. Ammonium chloride from nitride containing a large amount of unattacked magnesium.
   0.0630 gram. required 24.55 cub. centims. of silver nitrate = 66.30 per cent. of chlorine.

Taking for the atomic weights of hydrogen, H = 1.0082, of nitrogen, N = 14.04, and of chlorine, Cl = 35.46, the theoretical amount of chlorine in ammonium chloride is 66.27 per cent.

From these results—that nitrogen prepared from magnesium nitride obtained by passing "atmospheric" nitrogen over red-hot magnesium has the density of "chemical" nitrogen, and that ammonium chloride prepared from magnesium nitride contains practically the same percentage of chlorine as pure ammonium chloride—it may be concluded that red-hot magnesium withdraws from "atmospheric" nitrogen no substance other than nitrogen capable of forming a basic compound with hydrogen.

In a subsequent part of this paper, attention will again be called to this statement. (See addendum p. 240.)

2. Reasons for Suspecting a hitherto Undiscovered Constituent in Air.

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these the most likely appeared to be hydrogen, present in the lighter gas, in spite of the passage over red-hot cupric oxide. But, inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned; and, finally, it became
clear that the difference could not be accounted for by the presence of any known impurity. At this stage it seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules $N_2$ into detached atoms. In order to test this suggestion, both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behaviour of nitrogen is such as to suggest that dissociated atoms would possess a higher degree of activity, and that, even though they might be formed in the first instance, their life would probably be short. On standing, they might be expected to disappear, in partial analogy with the known behaviour of ozone. With this idea in view, a sample of chemically-prepared nitrogen was stored for eight months. But, at the end of this time, the density showed no sign of increase, remaining exactly as at first.*

Regarding it as established that one or other of the gases must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, one-half per cent. only by volume would be needed; or, if the density were but half as much again as that of nitrogen, then one per cent. would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means Graham succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contain an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. If, for example, the parts least disposed to penetrate porous walls were retained, the "nitrogen" derived from it by the usual processes should be heavier than that derived in like manner from unprepared air. This experiment, although in view from the first, was not executed until a later stage of the inquiry (§ 6), when results were

obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first question, it held out no prospect of isolating the new constituent of the atmosphere, and we therefore turned our attention in the first instance to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favour of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U-tube. This tube (M) was only about \( \frac{1}{10} \) inch in diameter, and the column of gas was usually about 1 inch in length. After describing some preliminary trials, Cavendish proceeds:—"I introduced into the tube a little soap-lees (potash), and then let up some dephlogisticated† and common air, mixed in the above mentioned proportions which rising to the top of the tube M, divided the soap-lees into its two legs. As fast as the air was diminished by the electric spark, I continued adding more of the same kind, till no further diminution took place: after which a little pure dephlogisticated air, and after that a little common air, were added, in order to see whether the cessation of diminution was not owing to some imperfection in the proportion of the two kinds of air to each other; but without effect. The soap-lees being then poured out of the tube, and separated from the quicksilver, seemed to be perfectly neutralised, and they did not at all discolour paper tinged with the juice of blue flowers. Being evaporated to dryness, they left a small quantity of salt, which was evidently nitre, as appeared by the manner in which paper, impregnated with a solution of it, burned."

Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we

---


† The explanation of combustion in Cavendish's day was still vague. It was generally imagined that substances capable of burning contained an unknown principle, to which the name 'phlogiston' was applied, and which escaped during combustion. Thus, metals and hydrogen and other gases were said to be 'phlogisticated' if they were capable of burning in air. Oxygen being non-inflammable was named 'dephlogisticated air,' and nitrogen, because it was incapable of supporting combustion, was named by Priestley 'phlogisticated air,' although up till Cavendish's time it had not been made to unite with oxygen.

The term used for oxygen by Cavendish is 'dephlogisticated air,' and for nitrogen, 'phlogisticated air.'—April, 1895.]
could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmosphere than that it is not diminished by lime-water, caustic alkalies, or nitrous air; that it is unfit to support fire or maintain life in animals; and that its specific gravity is not much less than that of common air; so that, though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and consequently, though it was reasonable to suppose, that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the whole is of this kind, or whether there are not in reality many different substances confounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompose it as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it and continued the spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than \( \frac{1}{136} \) of the bulk of the phlogisticated air let up into the tube; so that, if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than \( \frac{1}{136} \) part of the whole."

Although Cavendish was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of the "phlogisticated air," and contained the gas now called argon.

Cavendish gives data\(^*\) from which it is possible to determine the rate of absorption of the mixed gases in his experiment. The electrical machine used \(^*\) was one of Mr. Nairne's patent machines, the cylinder of which is 12\(\frac{1}{2}\) inches long and 7 in diameter. A conductor, 5 feet long and 6 inches in diameter, was adapted to it, and the ball which received the spark was placed two or three inches from another ball, fixed to the end of the conductor. Now, when the machine worked well, Mr. Gilpin supposes he got about two or three hundred sparks a minute, and the diminution of

\(^*\) 'Phil. Trans.,' vol. 78, p. 271, 1788.
the air during the half hour which he continued working at a time varied in general from 40 to 120 measures, but was usually greatest when there was most air in the tube, provided the quantity was not so great as to prevent the spark from passing readily." The "measure" spoken of represents the volume of one grain of quicksilver, or .0048 cub. centim., so that an absorption of one cub. centim. of mixed gas per hour was about the most favourable rate. Of the mixed gas about two-fifths would be nitrogen.


The concord between the determinations of density of nitrogen obtained from sources other than the atmosphere, having made it at least probable that some heavier gas exists in the atmosphere, hitherto undetected, it became necessary to submit atmospheric nitrogen to examination, with a view of isolating, if possible, the unknown and overlooked constituent, or it might be constituents.

Nitrogen, however, is an element which does not easily enter into direct combination with other elements; but with certain elements, and under certain conditions, combination may be induced. The elements which have been directly united to nitrogen are (a) boron, (b) silicon, (c) titanium, (d) lithium, (e) strontium and barium, (f) magnesium, (g) aluminium, (h) mercury, (i) manganese, (j) hydrogen, and (k) oxygen, the last two by help of an electrical discharge.

(a.) Nitride of boron was prepared by Wöhler and Deville* by heating amorphous boron to a white heat in a current of nitrogen. Experiments were made to test whether the reaction would take place in a tube of difficultly fusible glass; but it was found that the combination took place at a bright red heat to only a small extent, and that the boron, which had been prepared by heating powdered boron oxide with magnesium dust, was only superficially attacked. Boron is, therefore, not a convenient absorbent for nitrogen. [M. Moissan informs us that the reputation it possesses is due to the fact that early experiments were made with boron which had been obtained by means of sodium, and which probably contained a boride of that metal. —April, 1895.]

(b.) Nitride of silicon† also requires for its formation a white heat, and complete union is difficult to bring about. Moreover, it is not easy to obtain large quantities of silicon. This method was therefore not attempted.

(c.) Nitride of titanium is said to have been formed by Deville and Caron;‡ by heating titanium to whiteness in a current of nitrogen. This process was not tried by us. As titanium has an unusual tendency to unite with nitrogen, it might, perhaps, be worth while to set the element free in presence of atmospheric nitrogen, with a view to the absorption of the nitrogen. This has, in effect, been already done

* 'Annales de Chimie,' (3), 52, p. 82.
† Schützenberger, 'Comptes Rendus,' 89, 644.
‡ 'Annalen der Chemie u. Pharmacie,' 101, 350.
by Wöhler and Deville; they passed a mixture of the vapour of titanium chloride and nitrogen over red-hot aluminium, and obtained a large yield of nitride. It is possible that a mixture of the precipitated oxide of titanium with magnesium dust might be an effective absorbing agent at a comparatively low temperature. [Since writing the above we have been informed by M. Moissan that titanium, heated to 800°, burns brilliantly in a current of nitrogen. It might therefore be used with advantage to remove nitrogen from air, inasmuch as we have found that it does not combine with argon.—April, 1895.]

(d.), (e.) Lithium at a dull red heat absorbs nitrogen,† but the difficulty of obtaining the metal in quantity precludes its application. On the other hand, strontium and barium, prepared by electrolysing solutions of their chlorides in contact with mercury, and subsequently removing the mercury by distillation, are said by Maquenne‡ to absorb nitrogen with readiness. Although we have not tried these metals for removing nitrogen, still our experience with their amalgams has led us to doubt their efficacy, for it is extremely difficult to free them from mercury by distillation, and the product is a fused ingot, exposing very little surface to the action of the gas. The process might, however, be worth a trial.

Barium is the efficient absorbent for nitrogen when a mixture of barium carbonate and carbon is ignited in a current of nitrogen, yielding cyanide. Experiments have shown, however, that the formation of cyanides takes place much more readily and abundantly at a high temperature, a temperature not easily reached with laboratory appliances. Should the process ever come to be worked on a large scale, the gas rejected by the barium will undoubtedly prove a most convenient source of argon.

(f.) Nitride of magnesium was prepared by Deville and Caron (loc. cit.) during the distillation of impure magnesium. It has been more carefully investigated by Bregleb and Geuther,§ who obtained it by igniting metallic magnesium in a current of nitrogen. It forms an orange-brown, friable substance, very porous, and it is easily produced at a bright red heat. When magnesium, preferably in the form of thin turnings, is heated in a combustion tube in a current of nitrogen, the tube is attacked superficially, a coating of magnesium silicide being formed. As the temperature rises to bright redness, the magnesium begins to glow brightly, and combustion takes place, beginning at that end of the tube through which the gas is introduced. The combustion proceeds regularly, the glow extending down the tube, until all the metal has united with nitrogen. The heat developed by the combination is considerable, and the glass softens; but by careful attention and regulation of the rate of the current, the tube lasts out an operation. A piece of combustion tubing of the usual length for organic analysis packed tightly with magnesium turnings, and containing

* 'Annalen der Chemie u. Pharmacie,' 73, 34.
† Ouvrard, 'Comptes Rendus,' 114, 120.
‡ Ouvrard, 'Comptes Rendus,' 114, 25, and 220.
§ 'Annalen der Chemie u. Pharmacie,' 123, 228.
about 30 grams, absorbs between seven and eight litres of nitrogen. It is essential that oxygen be excluded from the tube, otherwise a fusible substance is produced, possibly nitrate, which blocks the tube. With the precaution of excluding oxygen, the nitride is loose and porous, and can easily be removed from the tube with a rod; but it is not possible to use a tube twice, for the glass is generally softened and deformed.

(g.) Nitride of aluminium has been investigated by Mallet.* He obtained it in crystals by heating the metal to whiteness in a carbon crucible. But aluminium shows no tendency to unite with nitrogen at a red heat, and cannot be used as an absorbent for the gas.

(h.) Gerresheim† states that he has induced combination between nitrogen and mercury; but the affinity between these elements is of the slightest, for the compound is explosive.

(i.) In addition to these, metallic manganese in a finely divided state has been shown to absorb nitrogen at a not very elevated temperature, forming a nitride of the formula Mn₃N₂‡.

(j.) [A mixture of nitrogen with hydrogen, standing over acid, is absorbed at a fair rate under the influence of electric sparks. But with an apparatus such as that shown in fig. 1, the efficiency is but a fraction (perhaps \( \frac{1}{3} \)) of that obtainable when oxygen is substituted for hydrogen and alkali for acid.—April, 1895.]


In our earliest attempts to isolate the suspected gas by the method of Cavendish, we used a Ruimkorf coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test-tube A, fig. 1, standing over a large quantity of weak alkali B, and the current was conveyed in wires insulated by U-shaped glass tubes CC passing through the liquid round the mouth of the test tube. The inner platinum ends DD of the wires were sealed into the glass insulating tubes, but reliance was not placed upon these sealings. In order to secure tightness in spite of cracks, mercury was placed in the bends. This disposition of the electrodes complicates the apparatus somewhat and entails the use of a large depth of liquid in order to render possible the withdrawal of the tubes, but it has the great advantage of dispensing with sealing electrodes of platinum into the principal vessel, which might give way and cause the loss of the experiment at the most inconvenient moment. With the given battery and coil a somewhat short spark, or arc, of about 5 millims. was found to be more favourable than a longer one. When the mixed gases were in the right proportion, the rate of absorption was about 30 cub. centims.

† ′Annalen der Chemie u. Pharmacie,′ 195, 373.
‡ O. Prelinger, ′Monatsl. f. Chemie,′ 15, 391.
per hour, or 30 times as fast as Cavendish could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 cub. centims. of air. To this, oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury,

![Diagram](image)

in which the volume was found to be 1'0 cub. centim. On treatment with alkaline pyrogallate, the gas shrank to 32 cub. centim. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favourable proportion.

The residue was then transferred to the test-tube with an addition of another 50 cub. centims. of air, and the whole worked up with oxygen as before. The residue was now 2'2 cub. centims., and, after removal of oxygen, 76 cub. centim.
Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapour) was unduly high. But any doubts that were felt upon this score were removed by comparison experiments in which the whole quantity of air operated on was very small. Thus, when a mixture of 5 cub. centims. of air with 7 cub. centims. of oxygen was sparked for one hour and a quarter, the residue was '47 cub. centim., and, after removal of oxygen, '06 cub. centim. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, but was in proportion to the amount of air operated upon.

No satisfactory examination of the residue which refused to be oxidised could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. The gas seemed to rebel against the law of addition. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a comparison with the air spectrum taken under similar conditions proved that, at any rate, the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

[The apparatus shown in fig. 1 has proved to be convenient for the purification of small quantities of argon, and for determinations of the amount of argon present in various samples of gas, e.g., in the gases expelled from solution in water. To set it in action an alternating current is much to be preferred to a battery and break. At the Royal Institution the primary of a small Ruhmkorff was fed from the 100-volt alternating current supply, controlled by two large incandescent lamps in series with the coil. With this arrangement the voltage at the terminals of the secondary, available for starting the sparks, was about 2000, and could be raised to 4000 by plugging out one of the lamps. With both lamps in use the rate of absorption of mixed gases was 80 cub. centims. per hour, and this was about as much as could well be carried out in a test-tube. Even with this amount of power it was found better to abandon the sealings at D. No inconvenience arises from the open ends, if the tubes are wide enough to ensure the liberation of any gas included over the mercury when they are sunk below the liquid.

The power actually expended upon the coil is very small. When the apparatus is at work the current taken is only 2·4 amperes. As regards the voltage, by far the greater part is consumed in the lamps. The efficient voltage at the terminals of the primary coil is best found indirectly. Thus, if A be the current in amperes, V the total voltage, $V_1$ the voltage at the terminals of the coil, $V_2$ that at the terminals of the lamps, the watts used are*  

W = \frac{A}{2V_2} (V^2 - V_2^2 - V_1^2).

In the present case a Cardew voltmeter gave \( V = 90^{1/2}, \ V_3 = 88 \); and \( V_1^2 \) in the formula may be neglected. Thus,

\[
W = \frac{A}{2V_2} (V + V_2) (V - V_3) = A (V - V_3)
\]

\[
= 2.4 \times 2.5 = 6.0 \text{ approximately.}
\]

The work consumed by the coil when the sparks are passing is, thus, less than \( \frac{1}{100} \) of a horse-power; but, in designing an apparatus, it must further be remembered that in order to maintain the arc, a pretty high voltage is required at the terminals of the secondary when no current is passing in it.—April, 1895.]

5. Early Experiments on Withdrawal of Nitrogen from Air by means of Red-hot Magnesium.

It having been proved that nitrogen, at a bright red heat, was easily absorbed by magnesium, best in the form of turnings, an attempt was successfully made to remove that gas from the residue left after eliminating oxygen from air by means of red-hot copper.

Fig. 2.

The preliminary experiment was made in the following manner:—A combustion tube, A, was filled with magnesium turnings, packed tightly by pushing them in with a rod. This tube was connected with a second piece of combustion tubing, B, by means of thick-walled india-rubber tubing, carefully wired; B contained copper oxide, and, in its turn, was connected with the tube CD, one-half of which contained soda-lime, previously ignited to expel moisture, while the other half was filled with phosphoric anhydride. E is a measuring vessel, and F is a gas-holder containing “atmospheric nitrogen.”
In beginning an experiment, the tubes were heated with long-flame burners, and pumped empty; a little hydrogen was formed by the action of the moisture on the metallic magnesium; it was oxidised by the copper oxide and absorbed by the phosphoric pentoxide. A gauge attached to the Sprengel's pump, connected with the apparatus, showed when a vacuum had been reached. A quantity of nitrogen was then measured in E, and admitted into contact with the red-hot magnesium. Absorption took place, rapidly at first and then slowly, as shown by the gauge on the Sprengel's pump. A fresh quantity was then measured and admitted, and these operations were repeated until no more could be absorbed. The system of tubes was then pumped empty by means of the Sprengel's pump, and the gas was collected. The magnesium tube was then detached and replaced by another. The unabsorbed gas was returned to the measuring-tube by a device shown in the figure (G) and the absorption recommenced. After 1094 cub. centims. of gas had been thus treated, there was left about 50 cub. centims. of gas, which resisted rapid absorption. It still contained nitrogen, however, judging by the diminution of volume which it experienced when allowed to stand in contact with red-hot magnesium. Its density was, nevertheless, determined by weighing a small bulb of about 40 cub. centims. capacity, first with air, and afterwards with the gas. The data are these:—

\[
\begin{array}{l}
(a.) \quad \text{Weight of bulb and air} - \text{that of glass counterpoise} \quad 0'8094 \\
\quad \quad \quad \text{alone} - \text{that of glass counterpoise} \quad 0'7588 \\
\quad \quad \quad \text{air} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \q
This result was encouraging, although weighted with the unavoidable error attaching to the weighing of a very small amount. Still the fact remains that the supposed nitrogen was heavier than air. It would hardly have been possible to make a mistake of 2.7 milligrams.

It is right here to place on record the fact that this first experiment was to a great extent carried out by Mr. Percy Williams, to whose skill in manipulation and great care its success is due, and to whom we desire here to express our thanks.

Experiments were now begun on a larger scale, the apparatus employed being shown in figs. 3 and 4.

Fig. 3.

A and B are large glass gas-holders of about 10 litres capacity. C is an arrangement by which gas could be introduced at will into the gas-holder A, either by means of an india-rubber tube slipped over the open end of the U-tube, or, as shown in the figure, from a test-tube. The tube D was half filled with soda-lime (a), half with phosphoric anhydride (b). Similarly, the tube E, which was kept at a red heat by means of the long-flame burner, was filled half with very porous copper (a), reduced from dusty oxide by heating in hydrogen, half with copper oxide in a granular form (b). The next tube, F, contained granular soda-lime, while G contained magnesium turn-

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1.29347</td>
<td>1.42961</td>
<td>1.25749</td>
<td>0.08991</td>
</tr>
</tbody>
</table>

This ratio gives for air the composition by volume—

| Oxygen . . . . . . . . . . | 20.91 per cent. |
| Nitrogen . . . . . . . . | 79.09 " |

a result verified by experiment.

It is, of course, to be understood that these densities of nitrogen refer to atmospheric nitrogen, that is, to air from which oxygen, water vapour, carbon dioxide, and ammonia have been removed.
A NEW CONSTITUENT OF THE ATMOSPHERE.

ings, also heated to bright redness by means of a long-flame burner. H contained phosphoric anhydride, and I soda-lime. All joints were sealed, excepting those connecting the hard-glass tubes E and G to the tubes next them.

The gas-holder A having been filled with nitrogen, prepared by passing air over red-hot copper, and introduced at C, the gas was slowly passed through the system of tubes into the gas-holder B, and back again. The magnesium in the tube G having then ceased to absorb was quickly removed and replaced by a fresh tube. This tube was of course full of air, and before the tube G was heated, the air was carried back from B towards A by passing a little nitrogen from right to left. The oxygen in the air was removed by the metallic copper, and the nitrogen passed into the gas-holder A, to be returned in the opposite direction to B.

Fig. 4.

In the course of about ten days most of the nitrogen had been absorbed. The magnesium was not always completely exhausted; usually the nitride presented the appearance of a blackish-yellow mass, easily shaken out of the tube. It is needless to say that the tube was always somewhat attacked, becoming black with a coating of magnesium silicide. The nitride of magnesium, whether blackish or orange, if left for a few hours exposed to moist air, was completely converted into white, dusty hydroxide, and during exposure it gave off a strong odour of ammonia. If kept in a stoppered bottle, however, it was quite stable.

It was then necessary, in order to continue the absorption, to carry on operations on a smaller scale, with precautions to exclude atmospheric air as completely as possible. There was at this stage a residue of 1500 cub. centims.

The apparatus was therefore altered to that shown in fig. 4, so as to make it possible to withdraw all the gas out of the gas-holder A.

The left-hand exit led to the Sprengel's pump; the compartment (a) of the drying-tube B was filled with soda-lime, and (b) with phosphoric anhydride. C is a
tube into which the gas could be drawn from the gas-holder A. The stop-cock, as shown, allows gas to pass through the horizontal tubes, and does not communicate with A; but a vertical groove allows it to be placed in communication either with the gas-holder, or with the apparatus to the right. The compartment (a) of the second drying-tube D contained soda-lime, and (b) phosphoric anhydride. The tube D communicated with a hard-glass tube E, heated over a long-flame burner; it was partly filled with metallic copper, and partly with copper oxide. This tube, as well as the tube F filled with magnesium turnings, was connected to the drying-tube with india-rubber. The gas then entered G, a graduated reservoir, and the arrangement H permitted the removal or introduction of gas from or into the apparatus. The gas was gradually transferred from the gas-holder to the tube C, and passed backwards and forwards over the red-hot magnesium until only about 200 cub. centims. were left. It was necessary to change the magnesium tube, which was made of smaller size than formerly, several times during the operation. This was done by turning out the long-flame burners and pumping off all gas in the horizontal tubes by means of the Sprengel's pump. This gas was carefully collected. The magnesium tube was then exchanged for a fresh one, and after air had been exhausted from the apparatus, nitrogen was introduced from the reservoir. Any gas evolved from the magnesium (and apparently there was always a trace of hydrogen, either occluded by the magnesium, or produced by the action of aqueous vapour on the metal) was oxidised by the copper oxide. Had oxygen been present, it would have been absorbed by the metallic copper, but the copper preserved its red appearance without alteration, whereas a little copper oxide was reduced during the series of operations. The gas, which had been removed by pumping, was reintroduced at H, and the absorption continued.

The volume of the gas was thus, as has been said, reduced to about 200 cub. centims. It would have been advisable to take exact measurements, but, unfortunately, some of the original nitrogen had been lost through leakage; and a natural anxiety to see if there was any unknown gas led to pushing on operations as quickly as possible.

The density of the gas was next determined. The bulb or globe in which the gas was weighed was sealed to a two-way stop-cock, and the weight of distilled and air-free water filling it at \(17 \cdot 15^\circ\) was 162.654 grms., corresponding to a capacity of 162.843 cub. centims. The shrinkage on removing air completely was 0.0212 cub. centim. Its weight, when empty, should therefore be increased by the weight of that volume of air, which may be taken as 0.000026 grm. This correction, however, is perhaps hardly worth applying in the present case.

The counterpoise was an exactly similar bulb of equal capacity, and weighing about 0.2 grm. heavier than the empty globe. The balance was a very sensitive one by Oertling, which easily registered one-tenth of a milligrm. By the process of swinging, one-hundredth of a milligrm. could be determined with fair accuracy.

In weighing the empty globe, 0.2 grm. was placed on the same pan as that which
hung from the end of the beam to which it was suspended, and the final weight was adjusted by means of a rider, or by small weights on the other pan. This process practically leads to weighing by substitution of gas for weights. The bulb was always handled with gloves, to avoid moisture or grease from the fingers.

Three experiments, of which it is unnecessary to give details, were made to test the degree of accuracy with which a gas could be weighed, the gas being dried air, freed from carbon dioxide. The mean result gave for the weight of one litre of air at 0° and 760 millims. pressure, 1.2935 grm. REGNAULT found 1.29340, a correction having been applied by Crafts to allow for the estimated alteration of volume caused by the contraction of his vacuous bulb. The mean result of determinations by several observers is 1.29347; while one of us found 1.29327.

The globe was then filled with the carefully dried gas.

Temperature, 18.80°. Pressure, 759.3 millims.
Weight of 162.843 cub. centims. of gas . . . . . . 0.21897 grm.
Weight of 1 litre gas at 0° and 760 millims. . . . . 1.4386 ,
Density, that of air compared with O, = 16, being 14.476 16.100 grms.

It is evident from these numbers that the dense constituent of the air was being concentrated. As a check, the bulb was pumped empty and again weighed; its weight was 0.21903 grm. This makes the density 16.105.

It appeared advisable to continue to absorb nitrogen from this gas. The first tube of magnesium removed a considerable quantity of gas; the nitride was converted into ammonium chloride, and the sample contained 66.30 per cent. of chlorine, showing, as has before been remarked, that if any of the heavier constituent of the atmosphere had been absorbed, it formed no basic compound with hydrogen. The second tube of magnesium was hardly attacked; most of the magnesium had melted, and formed a layer at the lower part of the tube. That which was still left in the body of the tube was black on the surface, but had evidently not been much attacked. The ammonium chloride which it yielded weighed only 0.0035 grm.

The density of the remaining gas was then determined. But as its volume was only a little over 100 cub. centims., the bulb, the capacity of which was 162 cub. centims., had to be filled at reduced pressure. This was easily done by replacing the pear-shaped reservoir of the mercury gas-holder by a straight tube, and noting the level of the mercury in the gas-holder and in the tube which served as a mercury reservoir against a graduated mirror-scale by help of a cathetometer at the moment of closing the stop-cock of the density bulb.

The details of the experiment are these:

Temperature, 19.12° C. Barometric pressure, 749.8 millims. (corr.).
Difference read on gas-holder and tube, 225.25 millims. (corr.).
Actual pressure, 524.55 millims.
Weight of 162·843 cub. centims. of gas . . . . . . 0·17913 grn.
Weight of 1 litre at 0° and 760 millims. pressure . . 1·7054 ,
Density . . . . . . . . . . . . . . . . . . . . . . 19·086 grms.

This gas is accordingly at least 19 times as heavy as hydrogen.
A portion of the gas was then mixed with oxygen, and submitted to a rapid
discharge of sparks for four hours in presence of caustic potash. It contracted, and
on absorbing the excess of oxygen with pyrogallate of potassium the contraction
amounted to 15·4 per cent. of the original volume. The question then arises, if the
gas contain 15·4 per cent. of nitrogen, of density 14·014, and 84·6 per cent. of other
gas, and if the density of the mixture were 19·086, what would be the density of the
other gas? Calculation leads to the number 20·0.
A vacuum-tube was filled with a specimen of the gas of density 19·086, and it
could not be doubted that it contained nitrogen, the bands of which were distinctly
visible. It was probable, therefore, that the true density of the pure gas lay not far
from 20 times that of hydrogen. At the same time many lines were seen which
could not be recognized as belonging to the spectrum of any known substance.
Such were the preliminary experiments made with the aid of magnesium to
separate from atmospheric nitrogen its dense constituent. The methods adopted in
preparing large quantities will be subsequently described.


It has already (§ 2) been suggested that if "atmospheric nitrogen" contains two
gases of different densities, it should be possible to obtain direct evidence of the fact
by the method of atmolysis. The present section contains an account of carefully
conducted experiments directed to this end.
The atmoliser was prepared (after Graham) by combining a number of "church-
warden" tobacco pipes. At first twelve pipes were used in three groups, each group
including four pipes connected in series. The three groups were then connected in
parallel, and placed in a large glass tube closed in such a way that a partial vacuum
could be maintained in the space outside the pipes by a water-pump. One end of
the combination of pipes was open to the atmosphere, or rather was connected with
the interior of an open bottle containing sticks of caustic alkali, the object being
mainly to dry the air. The other end of the combination was connected to a bottle
aspirator, initially full of water, and so arranged as to draw about two per cent. of
the air which entered the other end of the pipes. The gas collected was thus a very
small proportion of that which leaked through the pores of the pipes, and should be
relatively rich in the heavier constituents of the atmosphere. The flow of water
from the aspirator could not be maintained very constant, but the rate of two per
cent. was never much exceeded. The necessary four litres took about sixteen hours
to collect.
The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper followed by cupric oxide, ammonia by sulphuric acid, carbonic anhydride and moisture by potash and phosphoric anhydride.

The following are the results:

<table>
<thead>
<tr>
<th>Date</th>
<th>Weight of Gas</th>
<th>Ordinary Atmospheric Nitrogen</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Globe empty July 10, 14</td>
<td>2.81789</td>
<td>2.31016</td>
<td>+0.50781</td>
</tr>
<tr>
<td>Globe full September 15 (twelve pipes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Globe empty September 17</td>
<td>2.81345</td>
<td>2.31016</td>
<td>+0.00138</td>
</tr>
<tr>
<td>Globe full September 18 (twelve pipes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Globe empty September 21</td>
<td>2.82320</td>
<td>2.31016</td>
<td>+0.00273</td>
</tr>
<tr>
<td>Globe full September 20 (twelve pipes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Globe empty September 21, October 30</td>
<td>2.82306</td>
<td>2.31016</td>
<td>+0.00150</td>
</tr>
<tr>
<td>Globe full September 22 (twelve pipes)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mean excess of the four determinations is +0.00262 gram., or if we omit the first, which depended upon a vacuum weighing of two months old, +0.00187 gram.

The gas from prepared air was thus in every case denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share, and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To
meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments eight pipes were connected in simple series. The porous surface in operation was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions:

<table>
<thead>
<tr>
<th></th>
<th>Globe empty, October 30, November 5</th>
<th>Globe full, November 3 (eight pipes)</th>
<th>Weight of gas</th>
<th>Ordinary atmospheric nitrogen</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>2.82313</td>
<td>0.50930</td>
<td>2.31383</td>
<td>2.31016</td>
<td>+0.00367</td>
</tr>
<tr>
<td>Difference</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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The excess being larger than before is doubtless due to the greater efficiency of the atmolysing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric-nitrogen" is a mixture and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen apparatus. The advance of 3.7 mg. on the 11 mg., by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

7. Negative Experiments to Prove that Argon is not derived from Nitrogen or from Chemical Sources.

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments (§ 6), appeared overwhelming, we have thought it undesirable to shrink from any labour that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13, in which 3 litres of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. In the course of operations an
accident occurred, by which no gas could have been lost, but of such a nature that from 100 to 200 cub. centims. of air must have entered the working vessel. The gas remaining at the close of the large scale operations was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 cub. centims. This was transferred, and after treatment with alkaline pyrogallate to remove oxygen, measured 3:3 cub. centims. If atmospheric nitrogen had been employed, the final residue should have been about 30 cub. centims. Of the 3:3 cub. centims. actually left, a part is accounted for by the accident alluded to, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

In a second experiment of the same kind 5660 cub. centims. of nitrogen from ammonium nitrite were treated with oxygen in the large apparatus (fig. 7; § 8). The final residue was 3:5 cub. centims.; and as evidenced by the spectrum, it consisted mainly of argon.

The source of the residual argon is to be found in the water used for the manipulation of the large quantities of gas (6 litres of nitrogen and 11 litres of oxygen) employed. Unfortunately the gases had been collected by allowing them to bubble up into aspirators charged with ordinary water, and they were displaced by ordinary water. In order to obtain information with respect to the contamination that may be acquired in this way, a parallel experiment was tried with carbonic anhydride. Eleven litres of the gas, prepared from marble and hydrochloric acid with ordinary precautions for the exclusion of air, were collected exactly as oxygen was commonly collected. It was then transferred by displacement with water to a gas pipette charged with a solution containing 100 grms. of caustic soda. The residue which refused absorption measured as much as 110 cub. centims. In another experiment where the water employed had been partially de-aerated, the residue left amounted to 71 cub. centims., of which 26 cub. centims. were oxygen. The quantities of dissolved gases thus extracted from water during the collection of oxygen and nitrogen suffice to explain the residual argon of the negative experiments.

It may perhaps be objected that the impurity was contained in the carbonic anhydride itself as it issued from the generating vessel, and was not derived from the water in the gas-holder; and indeed there seems to be a general impression that it is difficult to obtain carbonic anhydride in a state of purity. To test this question, 18 litres of the gas, made in the same generator and from the same materials, were passed directly into the absorption pipette. Under these conditions, the residue was only 62 cub. centims., corresponding to 4 cub. centims. from 11 litres. The quantity of gas employed was determined by decomposing the resulting sodium carbonate with hydrochloric acid, allowance being made for a little carbonic anhydride contained in the soda as taken from the stock bottle. It will be seen that there is no difficulty in reducing the impurity to $\frac{1}{3000}$th, even when india-rubber connections are freely used, and no extraordinary precautions are taken. The large amount of impurity
found in the gas when collected over water must therefore have been extracted from the water.

A similar set of experiments was carried out with magnesium. The nitrogen, of which three litres were used, was prepared by the action of bleaching-powder on ammonium chloride. It was circulated in the usual apparatus over red-hot magnesium, until its volume had been reduced to about 100 cub. centims. An equal volume of hydrogen was then added, owing to the impossibility of circulating a vacuum. The circulation then proceeded until all absorption had apparently stopped. The remaining gas was then passed over red-hot copper oxide into the Sprengel's pump, and collected. As it appeared still to contain hydrogen, which had escaped oxidation, owing to its great rarefaction, it was passed over copper oxide for a second and a third time. As there was still a residue, measuring 12·5 cub. centims., the gas was left in contact with red-hot magnesium for several hours, and then pumped out; its volume was then 4·5 cub. centims. Absorption was, however, still proceeding, when the experiment terminated, for at a low pressure, the rate is exceedingly slow. This gas, after being sparked with oxygen contracted to 3·0 cub. centims., and on examination was seen to consist mainly of argon. The amount of residue obtainable from three litres of atmospheric nitrogen should have amounted to a large multiple of this quantity.

In another experiment, 15 litres of nitrogen prepared from a mixture of ammonium chloride and sodium nitrite by warming in a flask (some nitrogen having first been drawn off by a vacuum-pump, in order to expel all air from the flask and from the contained liquid) were collected over water in a large gas-holder. The nitrogen was not bubbled through the water, but was admitted from above, while the water escaped below. This nitrogen was absorbed by red-hot magnesium, contained in tubes heated in a combustion-furnace. The unabsorbed gas was circulated over red-hot magnesium in a special small apparatus, by which its volume was reduced to 15 cub. centims. As it was impracticable further to reduce the volume by means of magnesium, the residual 15 cub. centims. were transferred to a tube, mixed with oxygen, and submitted to sparking over caustic soda. The residue after absorption of oxygen, which undoubtedly consisted of pure argon, amounted to 3·5 cub. centims. This is one-fortieth of the quantity which would have been obtained from atmospheric nitrogen, and its presence can be accounted for, we venture to think, first from the water in the gas-holder, which had not been freed from dissolved gas by boiling in vacuo (it has already been shown that a considerable gain may ensue from this source), and second, from leakage of air which accidentally took place, owing to the breaking of a tube. The leakage may have amounted to 200 cub. centims., but it could not be accurately ascertained. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.
8. Separation of Argon on a Large Scale.

To separate nitrogen from "atmospheric nitrogen" on a large scale, by help of magnesium, several devices were tried. It is not necessary to describe them all in detail. Suffice it to say that an attempt was made to cause a store of "atmospheric nitrogen" to circulate by means of a fan, driven by a water-motor. The difficulty encountered here was leakage at the bearing of the fan, and the introduced air produced a cake which blocked the tube on coming into contact with the magnesium. It might have been possible to remove oxygen by metallic copper; but instead of thus complicating the apparatus, a water-injector was made use of to induce circulation. Here also it is unnecessary to enter into details. For, though the plan worked well, and although about 120 litres of "atmospheric nitrogen" were absorbed, the yield of argon was not large, about 600 cub. centims. having been collected. This loss was subsequently discovered to be due partially, at least, to the relatively high solubility of argon in water. In order to propel the gas over magnesium, through a long combustion-tube packed with turnings, a considerable water-pressure, involving a large flow of water, was necessary. The gas was brought into intimate contact with this water, and presuming that several thousand litres of water ran through the injector, it is obvious that a not inconsiderable amount of argon must have been dissolved. Its proportion was increasing at each circulation, and consequently its partial pressure also increased. Hence, towards the end of the operation, at least, there is every reason to believe that a serious loss had occurred.

It was next attempted to pass "atmospheric nitrogen" from a gas-holder first through a combustion tube of the usual length packed with metallic copper reduced from the oxide; then through a small U-tube containing a little water, which was intended as an index of the rate of flow; the gas was then dried by passage through tubes filled with soda-lime and phosphoric anhydride; and it next passed through a long iron tube (gas-pipe) packed with magnesium turnings, and heated to bright redness in a second combustion-furnace.

After the iron tube followed a second small U-tube containing water, intended to indicate the rate at which the argon escaped into a small gas-holder placed to receive it. The nitrogen was absorbed rapidly, and argon entered the small gas-holder. But there was reason to suspect that the iron tube is permeable by argon at a red heat. The first tube-full allowed very little argon to pass. After it had been removed and replaced by a second, the same thing was noticed. The first tube was difficult to clean; the nitride of magnesium forms a cake on the interior of the tube, and it was very difficult to remove it; moreover this rendered the filling of the tube very troublesome, inasmuch as its interior was so rough that the magnesium turnings could only with difficulty be forced down. However, the permeability to argon, if such be the case, appeared to have decreased. The iron tube was coated internally with a skin of magnesium nitride, which appeared to diminish its permeability to argon.
After all the magnesium in the tube had been converted into nitride (and this was easily known, because a bright glow proceeded gradually from one end of the tube to the other) the argon remaining in the iron tube was "washed" out by a current of nitrogen; so that after a number of operations, the small gas-holder contained a mixture of argon with a considerable quantity of nitrogen.

On the whole, the use of iron tubes is not to be recommended, owing to the difficulty in cleaning them, and the possible loss through their permeability to argon. There is no such risk of loss with glass tubes, but each operation requires a new tube, and the cost of the glass is considerable if much nitrogen is to be absorbed. Tubes of porcelain were tried; but the glaze in the interior is destroyed by the action of the red-hot magnesium, and the tubes crack on cooling.

By these processes 157 litres of "atmospheric nitrogen" were reduced in volume to about 2·5 litres in all of a mixture of nitrogen and argon. This mixture was afterwards circulated over red-hot magnesium, in order to remove the last portion of nitrogen.

![Diagram of apparatus](image)

As the apparatus employed for this purpose proved very convenient, a full description of its construction is here given. A diagram is shown in fig. 5, which sufficiently explains the arrangement of the apparatus. A is the circulator. It consists of a sort of Sprengel's pump (a) to which a supply of mercury is admitted from a small
reservoir (b). This mercury is delivered into a gas-separator (c), and the mercury overflows into the reservoir (d). When its level rises, so that it blocks the tube (f), it ascends in pellets or pistons into (e), a reservoir which is connected through (g) with a water-pump. The mercury falls into (b), and again passes down the Sprengel tube (a). No attention is, therefore, required, for the apparatus works quite automatically. This form of apparatus was employed several years ago by Dr. Collie.

The gas is drawn from the gas-holder B, and passes through a tube C, which is heated to redness by a long-flame burner, and which contains in one half metallic copper, and in the other half copper oxide. This precaution is taken in order to remove any oxygen which may possibly be present, and also any hydrogen or hydrocarbon. In practice, it was never found that the copper became oxidised, or the oxide reduced. It is, however, useful to guard against any possible contamination. The gas next traversed a drying-tube D, the anterior portion containing ignited soda-lime, and the posterior portion phosphoric anhydride. From this it passed a reservoir, D', from which it could be transferred, when all absorption had ceased, into the small gas-holder. It then passed through E, a piece of combustion-tube, drawn out at both ends, filled with magnesium turnings, and heated by a long-flame burner to redness. Passing through a small bulb, provided with electrodes, it again entered the fall tube.

After the magnesium tube E had done its work, the stop-cocks were all closed, and the gas was turned down, so that the burners might cool. The mixture of argon and nitrogen remaining in the system of tubes was pumped out by a Sprengel's pump through F, collected in a large test-tube, and reintroduced into the gas-holder B through the side-tube G, which requires no description. The magnesium tube was then replaced by a fresh one; the system of tubes was exhausted of air; argon and nitrogen were admitted from the gas-holder B; the copper-oxide tube and the magnesium tube were again heated; and the operation was repeated until absorption ceased. It was easy to decide when this point had been reached, by making use of the graduated cylinder H, from which water entered the gas-holder B. It was found advisable to keep all the water employed in these operations, for it had become saturated with argon. If gas was withdrawn from the gas-holder, its place was taken by this saturated water.

The absorption of nitrogen proceeds very slowly towards the end of the operation, and the diminution in volume of the gas is not greater than 4 or 5 cub. centims. per hour. It is, therefore, somewhat difficult to judge of the end-point, as will be seen when experiments on the density of this gas are described. The magnesium tube, towards the end of the operations, was made so hot that the metal was melted in the lower part of the tube, and sublimed in the upper part. The argon and residual nitrogen had, therefore, been thoroughly mixed with gaseous magnesium during its passage through the tube E.

To avoid possible contamination with air in the Sprengel's pump, the last portion
of gas collected from the system of tubes was not re-admitted to the gas-holder B, but was separately stored.

The crude argon was collected in two operations. First, the quantity made by absorption by magnesium in glass tubes with the water-pump circulator was purified. Later, after a second supply had been prepared by absorption in iron tubes, the mixture of argon and nitrogen was united with the first quantity and circulated by means of the mercury circulator, in the gas-holder B. Attention will be drawn to the particular sample of gas employed in describing further experiments made with the argon.

By means of magnesium, about 7 litres of nitrogen can be absorbed in an hour. The changing of the tubes of magnesium, however, takes some time; consequently, the largest amount absorbed in one day was nearly 30 litres.

At a later date a quantitative experiment was carried out on a large scale, the amount of argon from 100 litres of "atmospheric" nitrogen, measured at 20°, having been absorbed by magnesium, and the resulting argon measured at 12°. During the process of absorbing nitrogen in the combustion-furnace, however, one tube cracked, and it is estimated that about 4 litres of nitrogen escaped before the crack was noticed. With this deduction, and assuming that the nitrogen had been measured at 12°, 93·4 litres of atmospheric nitrogen were taken. The magnesium required for absorption weighed 409 grms. The amount required by theory should have been 285 grms.; but it must be remembered that in many cases the magnesium was by no means wholly converted into nitride. The first operation yielded about 3 litres of a mixture of nitrogen and argon, which was purified in the circulating apparatus. The total residue, after absorption of the nitrogen, amounted to 921 cub. centims. The yield is therefore 0·986 per cent.

At first no doubt the nitrogen gains a little argon from the water over which it stands. But, later, when the argon forms the greater portion of the gaseous mixture, its solubility in water must materially decrease its volume. It is difficult to estimate the loss from this cause. The gas-holder, from which the final circulation took place, held three litres of water. Taking the solubility of argon as 4 per cent., this would mean a loss of about 120 cub. centims. If this is not an over-estimate, the yield of argon would be increased to 1040 cub. centims., or 1·11 per cent. The truth probably lies between these two estimates.

It may be concluded, with probability, that the argon forms approximately 1 per cent. of the "atmospheric" nitrogen.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. An absorption of 30 cub. centims. of mixed gas means the removal of but 12 cub. centims. of nitrogen. At this rate 8 hours are required for the isolation of 1 cub. centim. of argon, supposed to be present in the proportion of 1 per cent.

In extending the scale of operations we had the great advantage of the advice of
Mr. Crookes, who a short time ago called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.* Mr. Crookes was kind enough to arrange an impromptu demonstration at his own house with a small alternating current plant, in which it appeared that the absorption of mixed gas was at the rate of 500 cub. centims. per hour, or nearly 20 times as fast as with the battery. The arrangement is similar to that first described by Spottiswoode.† The primary of a Ruhmkorff coil is connected directly with the alternator, no break or condenser being required; so that, in fact, the coil acts simply as a high potential transformer. When the arc is established the platinum terminals may be separated much beyond the initial striking distance.

The plant with which the large scale operations have been made consists of a De Meritens alternator, kindly lent by Professor J. J. Thomson, and a gas engine. As transformer, one of Swinburne's hedgehog pattern has been employed with success, but the ratio of transformation (24 : 1) is scarcely sufficient. A higher potential, although, perhaps, not more efficient, is more convenient. The striking distance is greater, and the arc is not so liable to go out. Accordingly most of the work to be described has been performed with transformers of the Ruhmkorff type.

The apparatus has been varied greatly, and it cannot be regarded as having even yet assumed a final form. But it will give a sufficient idea of the method if we describe an experiment in which a tolerably good account was kept of the air and oxygen employed. The working vessel was a glass flask, A (fig. 6), of about 1500 cub. centims. capacity, and stood, neck downwards, over a large jar of alkali, B. As in the small scale experiments, the leading-in wires were insulated by glass tubes, DD, suitably bent and carried through the liquid up the neck. For the greater part of the length iron wires were employed, but the internal extremities, EE, were of platinum, doubled upon itself at the terminals from which the discharge escaped. The glass protecting tubes must be carried up for some distance above the internal level of the liquid, but it is desirable that the arc itself should not be much raised above that level. A general idea of the disposition of the electrodes will be obtained from fig. 6. To ensure gas tightness the bends were occupied by mercury. A tube, C2, for the supply or withdrawal of gas was carried in the same way through the neck.

The Ruhmkorff employed in this operation was one of medium size. When the mixture was rightly proportioned and the arc of full length, the rate of absorption was about 700 cub. centims. per hour. A good deal of time is lost in starting, for, especially when there is soda on the platinums, the arc is liable to go out if lengthened prematurely. After seven days the total quantity of air let in amounted to 7925 cub. centims., and of oxygen (prepared from chlorate of potash) 9137 cub. centims. On

* 'Chemical News,' vol. 65, p. 301, 1892.
† "A Mode of Exciting an Induction-coil." 'Phil. Mag.,' vol. 8, p. 300, 1879.
the eighth and ninth days oxygen alone was added, of which about 500 cub. centims. was consumed, while there remained about 700 cub. centims in the flask. Hence the proportion in which the air and oxygen combined was as 70:96. On the eighth day there was about three hours' work, and the absorption slackened off to about one quarter of the previous rate. On the ninth day (September 8) the rate fell off still more, and after three hours' work became very slow. The progress towards removal of nitrogen was examined from time to time with the spectroscope, the points being approximated and connected with a small Leyden jar. At this stage the yellow nitrogen line was faint, but plainly visible. After about four hours' more work, the yellow line had disappeared, and for two hours there had been no visible contraction. It will be seen that the removal of the last part of the nitrogen was very slow, mainly on account of the large excess of oxygen present.
The final treatment of the residual 700 cub. centims. of gas was on the model of the small scale operations already described (§ 4). By means of a pipette the gas was gradually transferred to a large test-tube standing over alkali. Under the influence of sparks (from battery and coil) passing all the while, the superfluous oxygen was consumed with hydrogen fed in slowly from a voltameter. If the nitrogen had been completely removed, and if there were no unknown ingredient in the atmosphere, the volume under this treatment should have diminished without limit. But the contraction stopped at a volume of 65 cub. centims., and the volume was taken backwards and forwards through this as a minimum by alternate treatment with oxygen and hydrogen added in small quantities, with prolonged intervals of sparking. Whether the oxygen or the hydrogen were in excess could be determined at any moment by a glance at the spectrum. At the minimum volume the gas was certainly not hydrogen or oxygen. Was it nitrogen? On this point the testimony of the spectroscope was equally decisive. No trace of the yellow nitrogen line could be seen even with a wide slit and under the most favourable conditions.

When the gas stood for some days over water the nitrogen line again asserted itself, and many hours of sparking with a little oxygen were required again to get rid of it. As it was important to know what proportions of nitrogen could be made visible in this way, a little air was added to gas that had been sparked for some time subsequently to the disappearance of nitrogen in its spectrum. It was found that about 1½ per cent. was clearly, and about 3 per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar in connection with the secondary terminals.

When we attempt to increase the rate of absorption by the use of a more powerful electric arc, further experimental difficulties present themselves. In the arrangement already described, giving an absorption of 700 cub. centims. per hour, the upper part of the flask becomes very hot. With a more powerful arc the heat rises to such a point that the flask is filled with steam and the operation comes to a standstill.

It is necessary to keep the vessel cool by either the external or internal application of liquid to the upper surface upon which the hot gases from the arc impinge. One way of effecting this is to cause a small fountain of alkali to impinge on the top of the flask, so as to wash the whole of the upper surface. This plan is very effective, but it is open to the objection that a break-down would be disastrous, and it would involve special arrangements to avoid losing the argon by solution in the large quantity of alkali required. It is simpler in many respects to keep the vessel cool by immersing it in a large body of water, and the inverted flask arrangement (fig. 6) has been applied in this manner. But, on the whole, it appears to be preferable to limit the application of the cooling water to the upper part of the external surface, building up for this purpose a suitable wall of sheet lead cemented round the glass. The most
convenient apparatus for large-scale operations that has hitherto been tried is shown in the accompanying figure (fig. 7).

The vessel A is a large globe of about 6 litres capacity, intended for demonstrating the combustion of phosphorus in oxygen gas, and stands in an inclined position. It is about half filled with a solution of caustic soda. The neck is fitted with a rubber stopper, B, provided with four perforations. Two of these are fitted with tubes, C, D, suitable for the supply or withdrawal of gas or liquid. The other two allow the passage of the stout glass tubes, E, F, which contain the electrodes. For greater security against leakage, the interior of these tubes is charged with water, held in place by small corks, and the outer ends are cemented up. The electrodes are formed of stout iron wires terminated by thick platinums, G, H, triply folded together, and welded at the ends. The lead walls required to enclose the cooling water are partially shown at I. For greater security the india-rubber cork is also drowned in water, held in place with the aid of sheet-lead. The lower part of the globe is occupied by about 3 litres of a 5 per cent. solution of caustic soda, the solution rising to within about half-an-inch of the platinum terminals. With this apparatus an absorption of 3 litres of mixed gas per hour can be attained,—about 3000 times the rate at which Cavendish could work.

When it is desired to stop operations, the feed of air (or of chemical nitrogen in blank experiments) is cut off, oxygen alone being supplied as long as any visible absorption occurs. Thus at the close the gas space is occupied by argon and oxygen with such nitrogen as cannot readily be taken up in a condition of so great dilution.
The oxygen, being too much for convenient treatment with hydrogen, was usually absorbed with copper and ammonia, and the residual gas was then worked over again as already described in an apparatus constructed upon a smaller scale.

It is worthy of notice that with the removal of the nitrogen, the arc-discharge from the dynamo changes greatly in appearance, bridging over more directly and in a narrower band from one platinum to the other, and assuming a beautiful sky-blue colour, instead of the greenish hue apparent so long as oxidation of nitrogen is in progress.

In all the large-scale experiments, an attempt was made to keep a reckoning of the air and oxygen employed, in the hope of obtaining data as to the proportional volume of argon in air, but various accidents too often interfered. In one successful experiment (January, 1895), specially undertaken for the sake of measurement, the total air employed was 9250 cub. centims., and the oxygen consumed, manipulated with the aid of partially de-aerated water, amounted to 10,820 cub. centims. The oxygen contained in the air would be 1942 cub. centims.; so that the quantities of "atmospheric nitrogen" and of total oxygen which enter into combination would be 7308 cub. centims., and 12,762 cub. centims. respectively. This corresponds to N + 1 750—the oxygen being decidedly in excess of the proportion required to form nitrous acid—2HNO₂, or H₂O + N₂ + 3O. The argon ultimately found on absorption of the excess of oxygen was 75 0 cub. centims., reduced to conditions similar to those under which the air was measured, or a little more than 1 per cent. of the "atmospheric nitrogen" used. It is probable, however, that some of the argon was lost by solution during the protracted operations required in order to get quit of the last traces of nitrogen.

[In recent operations at the Royal Institution, where a public supply of alternating current at 100 volts is available, the scale of the apparatus has been still further increased.

The capacity of the working vessel is 20 litres, of which about one half is occupied by a strong solution of caustic soda. The platinum terminals are very massive, and the flame rising from them is prevented from impinging directly upon the glass by a plate of platinum held over it and supported by a wire which passes through the rubber cork. In the electrical arrangements we have had the advantage of Mr. Swinburne's advice. The transformers are two of the "hedgehog" pattern, the thick wires being connected in parallel and the thin wires in series. In order to control the current taken when the arc is short or the platinums actually in contact, a choking-coil, provided with a movable core of fine iron wires, is inserted in the thick wire circuit. In normal working the current taken from the mains is about 22 amperes, so that some 2 ½ h. p. is consumed. At the same time the actual voltage at the platinum terminals is 1500. When the discharge ceases, the voltage at the platinum rises to 3000, which is the force actually available for re-starting the discharge if momentarily stopped.

* A still higher voltage on open circuit would be preferable.
With this discharge, the rate of absorption of mixed gases is about 7 litres per hour. When the argon has accumulated to a considerable extent, the rate falls off, and after several days' work, about 6 litres per hour becomes the maximum. In commencing operations it is advisable to introduce, first, the oxygen necessary to combine with the already included air, after which the feed of mixed gases should consist of about 11 parts of oxygen to 9 parts of air. The mixed gases may be contained in a large gas-holder, and then, the feed being automatic, very little attention is required. When it is desired to determine the rate of absorption, auxiliary gas-holders of glass, graduated into litres, are called into play. If the rate is unsatisfactory, a determination may be made of the proportion of oxygen in the working vessel, and the necessary gas, air, or oxygen, as the case may be, introduced directly.

In re-starting the arc after a period of intermission, it is desirable to cut off the connection with the principal gas-holder. The gas (about two litres in amount) ejected from the working vessel by the expansion is then retained in the auxiliary holder, and no argon finds its way further back. The connection between the working vessel and the auxiliary holder should be made without india-rubber, which is liable to be attacked by the ozonized gases.

The apparatus has been kept in operation for fourteen hours continuously, and there should be no difficulty in working day and night. An electric signal could easily be arranged to give notice of the extinction of the arc, which sometimes occurs unexpectedly; or an automatic device for re-striking the arc could be contrived.—April, 1895.]


A first estimate of the density of argon prepared by the oxygen method was founded upon the data recorded already respecting the volume present in air, on the assumption that the accurately known densities of "atmospheric" and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidised except nitrogen. Thus, if

\[ D = \text{density of chemical nitrogen}, \]
\[ D' = \text{atmospheric nitrogen}, \]
\[ d = \text{argon}, \]
\[ \alpha = \text{proportional volume of argon in atmospheric nitrogen}, \]

the law of mixtures gives

\[ \alpha d + (1 - \alpha) D = D \]

or

\[ d = D + (D' - D)/\alpha. \]
In this formula \(D' = D\) and \(\alpha\) are both small, but they are known with fair accuracy. From the data already given for the experiment of September 8th
\[
\alpha = \frac{65}{0.70 \times 7925} = 0.0104 ;
\]
whence, if on an arbitrary scale of reckoning \(D = 2.2990, D' = 2.3102\), we find \(d = 3.378\). Thus if \(N_2\) be 14, or \(O_2\) be 16, the density of argon is 20.6.

Again, from the January experiment,
\[
\alpha = \frac{75.0}{7308} = 0.0103 ;
\]
whence, if \(N = 14\), the density of argon is 20.6, as before. There can be little doubt, however, that these numbers are too high, the true value of \(\alpha\) being greater than is supposed in the above calculations.

A direct determination by weighing is desirable, but hitherto it has not been feasible to collect by this means sufficient to fill the large globe (§ 1) employed for other gases. A mixture of about 400 cub. centims. of argon with pure oxygen, however, gave the weight 2.7315, 0.1045 in excess of the weight of oxygen, viz., 2.6270. Thus, if \(\alpha\) be the ratio of the volume of argon to the whole volume, the number for argon will be
\[
2.6270 + 0.1045/\alpha.
\]

The value of \(\alpha\), being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave \(\alpha = 0.1845\); whence, for the weight of the gas we get 3.193; so that if \(O = 16\), the density of the gas would be 19.45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19.7, which may be taken as the density of pure argon resulting from this determination.*

10. Density of Argon Prepared by means of Magnesium.†

It has already been stated that the density of the residual gas from the first and preliminary attempt to separate oxygen and nitrogen from air by means of magnesium was 19.086, and allowing for contraction on sparking with oxygen the density is calculable as 20.01. The following determinations of density were also made:—

(a.) After absorption in glass tubes, the water circulator having been used, and subsequent circulation by means of mercury circulator until rate of contraction had

* [The proportion of nitrogen (4 or 5 per cent. of the volume) was estimated from the appearance of the nitrogen lines in the spectrum, these being somewhat more easily visible than when 3 per cent. of nitrogen was introduced into pure argon (§ 8).—April, 1895.]
† See Addendum, p. 237.
become slow, 162.843 cub. centims., measured at 757.7 millims. (corr.) pressure, and 16.81° C., weighed 0.2683 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . . 1.7543 grms.
Density compared with hydrogen (O = 16) . . . 19.63 "

This gas was again circulated over red-hot magnesium for two days. Before circulation it contained nitrogen as was evident from its spectrum; after circulating, nitrogen appeared to be absent, and absorption had completely stopped. The density was again determined.

(b.) 162,843 cub. centims., measured at 745.4 millims. (corr.) pressure, and 17.25° C., weighed 0.2785 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . . 1.8206 grms.
Density compared with hydrogen (O = 16) . . . 20.38 "

Several portions of this gas, having been withdrawn for various purposes, were somewhat contaminated with air, owing to leakage, passage through the pump, &c. All these portions were united in the gas-holder with the main stock, and circulated for eight hours, during the last three of which no contraction occurred. The gas removed from the system of tubes by the mercury-pump was not restored to the gas-holder, but kept separate.

(c.) 162.843 cub. centims., measured at 758.1 millims. (corr.) pressure, and 17.09° C., weighed 0.27705 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . . 1.8124 grms.
Density compared with hydrogen (O = 16) . . . 20.28 "

The contents of the gas-holder were subsequently increased by a mixture of nitrogen and argon from 37 litres of atmospheric nitrogen, and after circulating, density was determined. The absorption was however not complete.

(d.) 162.843 cub. centims., measured at 767.6 millims. (corr.) pressure, and 16.31° C., weighed 0.2703 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . . 1.742 grms.
Density compared with hydrogen (O = 16) . . . 19.49 "

The gas was further circulated, until all absorption had ceased. This took about six hours. Density was again determined.

(e.) 162.843 cub. centims. measured at 767.7 millims. (corr.) pressure, and 15.00° C., weighed 0.2773 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . . 1.7784 grms.
Density compared with hydrogen (O = 16) . . . 19.90 "
(f.) A second determination was carried out, without further circulation. 162.843 cub. centims. measured at 769.0 millims. (corr.) pressure, and 16.00° C., weighed 0.2757 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . . 1.7713 grms.
Density compared with hydrogen (O = 16) . . . 19.82 "

(g.) After various experiments had been made with the same sample of gas, it was again circulated until all absorption ceased. A vacuum-tube was filled with it, and showed no trace of nitrogen.

The density was again determined:—
162.843 cub. centims. measured at 750 millims. (corr.) pressure, and at 15.62° C., weighed 0.26915 grm.

Weight of 1 litre at 0° and 760 millims. . . . 1.7707 grms.
Density compared with hydrogen (O = 16) . . . 19.82 "

These comprise all the determinations of density made. It should be stated that there was some uncertainty discovered later about the weight of the vacuous globe in (b) and (c). Rejecting these weighings, the mean of (e), (f), and (g) is 19.88. The density may be taken as 19.9, with approximate accuracy.

It is better to leave these results without comment at this point, and to return to them later.

11. Spectrum of Argon.

Vacuum tubes were filled with argon prepared by means of magnesium at various stages in this work, and an examination of these tubes has been undertaken by Mr. Crookes, to whom we wish to express our cordial thanks for his kindness in affording us helpful information with regard to its spectrum. The first tube was filled with the early preparation of density 19.09, which obviously contained some nitrogen. A photograph of the spectrum was taken, and compared with a photograph of the spectrum of nitrogen, and it was at once evident that a spectrum different from that of nitrogen had been registered.

Since that time many other samples have been examined.

The spectrum of argon, seen in a vacuum tube of about 3 millims. pressure, consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas when examined in this way. Mr. Crookes, who gives a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines as well as of some others next to be described; they are respectively 696.56 and 703.64 × 10⁻⁶ millim.

Besides these red lines, a bright yellow line, more refrangible than the sodium line,
occurs at 603.84. A group of five bright green lines occurs next, besides a number of less intensity. Of this group of five, the second, which is perhaps the most brilliant, has the wave-length 561.00. There is next a blue, or blue-violet, line of wave-length 470.2 and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420.0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are only to be seen at atmospheric pressure when a very powerful jar-discharge is passed through argon. The spectrum, seen under these conditions, has been examined by Professor Schuster. The most characteristic lines are perhaps those in the neighbourhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water-vapour. The approximate wave-lengths are:

\[
\begin{align*}
487.91 & \quad \text{Strong} \\
(486.07) & \quad \text{F} \\
484.71 & \quad \text{Not quite so strong} \\
480.52 & \quad \text{Strong} \\
476.50 & \quad \text{F} \\
473.53 & \quad \text{Fairly strong characteristic triplet} \\
472.56 & \quad \text{F}
\end{align*}
\]

It is necessary to anticipate Mr. Crookes's communication, and to state that when the current is passed from the induction-coil in one direction, that end of the capillary tube next the positive pole appears a redder, and that next the negative a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. C. Baly,* who has noticed a similar phenomenon, attributes it to the presence of two gases. The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

A comparison was made of the spectrum seen in a vacuum tube with the spectrum in a "plenum" tube, i.e., one filled at atmospheric pressure. Both spectra were thrown into a field at the same time. It was evident that they were identical, although the relative strengths of the lines were not always the same. The seventeen most striking lines were absolutely coincident.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the

---

* 'Proc. Phys. Soc.,' 1893, p. 147. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other, and appears in the negative glow."
discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube, with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen it is true, but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium in vacuo, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking air-nitrogen with oxygen, in presence of caustic soda solution.

Professor Schuster has also found the principal lines identical in the spectra of the two gases, when taken from the jar discharge at atmospheric pressure.


The tendency of the gas to disappear when manipulated over water in small quantities having suggested that it might be more than usually soluble in that liquid, special experiments were tried to determine the degree of solubility.

The most satisfactory measures relating to the gas isolated by means of oxygen were those of September 28. The sample contained a trace of oxygen, and (as judged by the spectrum) a residue of about 2 per cent. of nitrogen. The procedure and the calculations followed pretty closely the course marked out by Bunsen, and it is scarcely necessary to record the details. The quantity of gas operated upon was about 4 cub. centims., of which about 1½ cub. centims. were absorbed. The final result for the solubility was 3.94 per 100 of water at 12° C., about 2½ times that of nitrogen. Similar results have been obtained with argon prepared by means of magnesium. At a temperature of 13.9°, 131 arbitrary measures of water absorbed 5.3 of argon. This corresponds to a solubility in distilled water, previously freed from dissolved gas by boiling in vacuo for a quarter of an hour, and admitted to the tube containing argon without contact with air, of 4.05 cub. centims. of argon per 100 of water.

The fact that the gas is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain water. Experiment has confirmed this anticipation. Some difficulty was at first experienced in collecting a sufficiency for the weighings in the large globe of nearly 2 litres capacity. Attempts at extraction by means of a Töpler pump without heat were not very successful. It was necessary to operate upon large quantities of water, and then the pressure of the liquid itself acted as an obstacle to the liberation of gas from all except the upper layers. Tapping the vessel with a stick of wood promotes the liberation of gas in a

* 'Gasometry,' p. 141.
remarkable manner, but to make this method effective, some means of circulating the water would have to be introduced.

The extraction of the gases by heat proved to be more manageable. Although a large quantity of water has to be brought to or near 100° C., a prolonged boiling is not necessary, as it is not a question of collecting the whole of the gas contained in the water. The apparatus employed, which worked very well after a little experience, will be understood from the accompanying figure. The boiler A was constructed

Fig. 8.

from an old oil-can, and was heated by an ordinary ring Bunsen burner. For the supply and removal of water, two co-axial tubes of thin brass, and more than four feet in length, were applied upon the regenerative principle. The outgoing water flowed in the inner tube BC, continued from C to D by a prolongation of composition tubing. The inflowing water from a rain-water cistern was delivered into a glass tube at E, and passed through a brass connecting tube FG into the narrow annular space between the two principal tubes GH. The neck of the can was fitted with an india-rubber cork and delivery-tube, by means of which the gases were collected in
The ordinary way. Any carbonic anhydride was removed by alkali before passage into the glass aspirating bottles used as gas-holders.

The convenient working of this apparatus depends very much upon the maintenance of a suitable relation between the heat and the supply of water. It is desirable that the water in the can should actually boil, but without a great development of steam; otherwise not only is there a waste of heat, and thus a smaller yield of gas, but the inverted flask used for the collection of the gas becomes inconveniently hot and charged with steam. It was found desirable to guard against this by the application of a slow stream of water to the external surface of the flask. When the supply of water is once adjusted, nearly half a litre of gas per hour can be collected with very little attention.

The gas, of which about four litres are required for each operation, was treated with red-hot copper, cupric oxide, sulphuric acid, potash, and finally phosphoric anhydride, exactly as atmospheric nitrogen was treated in former weighings. The weights found, corresponding to those recorded in §1, were on two occasions, 2.3221 and 2.3227, showing an excess of 24 milligrams above the weight of true nitrogen. Since the corresponding excess for atmospheric nitrogen is 11 milligrams, we conclude that the water-nitrogen is relatively twice as rich in argon.

Unless some still better process can be found, it may be desirable to collect the gases ejected from boilers, or from large supply pipes which run over an elevation, with a view to the preparation of argon upon a large scale.

The above experiments relate to rain water. As regards spring water, it is known that many thermal springs emit considerable quantities of gas, hitherto regarded as nitrogen. The question early occurred to us as to what proportion, if any, of the new gas was contained therein. A notable example of a nitrogen spring is that at Bath, examined by Daubeney in 1833. With the permission of the authorities of Bath, Dr. Arthur Richardson was kind enough to collect for us about 10 litres of the gases discharged from the King's Spring. A rough analysis on reception showed that it contained scarcely any oxygen and but little carbonic anhydride. Two determinations of density were made, the gas being treated in all respects as air, prepared by diffusion and unprepared, were treated for the isolation of atmospheric nitrogen. The results were :

<table>
<thead>
<tr>
<th>Date</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 29</td>
<td>2.30513</td>
</tr>
<tr>
<td>November 7</td>
<td>2.30532</td>
</tr>
<tr>
<td>Mean</td>
<td>2.30522</td>
</tr>
</tbody>
</table>

The weight of the "nitrogen" from the Bath gas is thus about halfway between that of chemical and "atmospheric" nitrogen, suggesting that the proportion of argon is less than in air, instead of greater as had been expected.
A single experiment was made with an early sample of gas, of density 19.1, which certainly contained a considerable amount of nitrogen. On compressing it in a pressure apparatus to between 80 and 100 atmospheres pressure, and cooling to −90° by means of boiling nitrous oxide, no appearance of liquefaction could be observed. As the critical pressure was not likely to be so high as the pressure to which it had been exposed, the non-liquefaction was ascribed to insufficient cooling.

This supposition turned out to be correct. For, on sending a sample to Professor Olszewski, the author of most of the accurate measurements of the constants of gases at low temperatures, he was kind enough to submit it to examination. His results are published elsewhere; but, for convenience of reference, his tables, showing vapour-pressures, and giving a comparison between the constants of argon and those of other gases, are here reproduced.

VAPOUR-PRESSIONS.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>−186.9</td>
<td>740.5</td>
<td>−136.2</td>
<td>27.3</td>
<td>−129.4</td>
<td>35.8</td>
</tr>
<tr>
<td>−139.1</td>
<td>23.7</td>
<td>−135.1</td>
<td>29.0</td>
<td>−128.6</td>
<td>38.0</td>
</tr>
<tr>
<td>−138.3</td>
<td>25.3</td>
<td>−134.4</td>
<td>29.8</td>
<td>−121.0</td>
<td>50.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas</th>
<th>Critical temperature</th>
<th>Critical pressure</th>
<th>Boiling-point</th>
<th>Freezing-point</th>
<th>Density of gas</th>
<th>Density of liquid at boiling-point</th>
<th>Colour of liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen, H₂</td>
<td>Below −2200°C</td>
<td>20.0 atms.</td>
<td>19.4</td>
<td>21.4</td>
<td>60</td>
<td>14</td>
<td>Colourless</td>
</tr>
<tr>
<td>Nitrogen, N₂</td>
<td>−146.0</td>
<td>35.0 atms.</td>
<td>−19.0</td>
<td>−21.0</td>
<td>100</td>
<td>14</td>
<td>Colourless</td>
</tr>
<tr>
<td>Carbon monoxide, CO</td>
<td>−139.5</td>
<td>35.5 atms.</td>
<td>−19.0</td>
<td>−20.7</td>
<td>100</td>
<td>14</td>
<td>Colourless</td>
</tr>
<tr>
<td>Argon, Ar</td>
<td>−121.0</td>
<td>50.6 atms.</td>
<td>−18.6</td>
<td>−19.6</td>
<td>19.9</td>
<td>1.5</td>
<td>Colourless</td>
</tr>
<tr>
<td>Oxygen, O₂</td>
<td>−118.8</td>
<td>50.8 atms.</td>
<td>−18.2</td>
<td>16</td>
<td>1.124</td>
<td>Bluish</td>
<td></td>
</tr>
<tr>
<td>Nitric oxide, NO</td>
<td>−93.5</td>
<td>71.2 atms.</td>
<td>−15.3</td>
<td>−16.7</td>
<td>138</td>
<td>15</td>
<td>Colourless</td>
</tr>
<tr>
<td>Methane, CH₄</td>
<td>−81.8</td>
<td>54.9 atms.</td>
<td>−16.4</td>
<td>−18.5</td>
<td>80</td>
<td>0.415</td>
<td>Colourless</td>
</tr>
</tbody>
</table>

14. The ratio of the Specific Heats of Argon.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that from the velocity of sound, the ratio of the specific heat at constant pressure to that at constant volume can be deduced by means of the equation

* See Addendum, p. 239.
\[ n \lambda = v = \sqrt{\left( \frac{c}{d} (1 + \alpha t) \frac{C_p}{C_v} \right)} \]

where \( n \) is the frequency, \( \lambda \) is the wave-length of sound, \( v \) its velocity, \( c \) the isothermal elasticity, \( d \) the density, \( (1 + \alpha t) \) the temperature-correction, \( C_p \) the specific heat at constant pressure, and \( C_v \) that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation and in using the same sound, many of these factors disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by the simple proportion

\[ \lambda^2 d : \lambda'^2 d' : : 1.408 : x, \]

where for example \( \lambda \) and \( d \) refer to air, of which the ratio is 1.408, according to the mean of observations by Röntgen (1.4053), Wüllner (1.4053), Kayser (1.4106), and Jamin and Richard (1.41).

The apparatus employed, although in principle the same as that usually employed, differed somewhat from the ordinary pattern, inasmuch as the tube was a narrow one, of 2 millims. bore, and the vibrator consisted of a glass rod, sealed into one end of the tube, so that about 15 centims. projected outside the tube, while 15 centims. was contained in the tube. By rubbing the projecting part longitudinally with a rag wet with alcohol, vibrations of exceedingly high pitch of the gas contained in the tube took place, causing waves which registered their nodes by the usual device of lycopodium powder. The temperature was that of the atmosphere and varied little from 17·5°; the pressure was also atmospheric, and varied only one millim. during the experiments. Much of the success of these experiments depends on so adjusting the length of the tube as to secure a good echo, else the wave-heaps are indistinct. But this is easily secured by attaching to its open end a piece of thick-walled india-rubber tubing, which can be closed by a clip at a spot which is found experimentally to produce good heaps at the nodes.

The accuracy of this instrument has frequently been tested; but fresh experiments were made with air, carbon dioxide, and hydrogen, so as to make certain that reasonably reliable results were obtainable. Of these an account is here given.

<table>
<thead>
<tr>
<th>Gas in tube</th>
<th>Number of observations</th>
<th>Half-wave-length</th>
<th>Ratio ( \frac{C_p}{C_v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I.</td>
<td>II.</td>
<td>I.</td>
</tr>
<tr>
<td>Air</td>
<td>3</td>
<td>2</td>
<td>19.60</td>
</tr>
<tr>
<td>CO₂</td>
<td>3</td>
<td>..</td>
<td>15.11</td>
</tr>
<tr>
<td>H₂</td>
<td>3</td>
<td>..</td>
<td>73.6</td>
</tr>
</tbody>
</table>

To compare these results with those of previous observers, the following numbers
were obtained for carbon dioxide:—Cazin, 1.291; Röntgen, 1.305; De Lucchi, 1.292; Müller, 1.265; Wüllner, 1.311; Dulong, 1.339; Masson, 1.274; Regnault, 1.268; Amagat, 1.299; and Jamin and Richard, 1.29. It appears just to reject Dulong's number, which deviates so markedly from the rest; the mean of those remaining is 1.288, which is in sufficient agreement with that given above. For the ratio of the specific heats of hydrogen, we have:—Cazin, 1.410; Röntgen, 1.385; Dulong, 1.407; Masson, 1.401; Regnault, 1.400; and Jamin and Richard, 1.410. The mean of these numbers is 1.402. This number appears to differ considerably from the one given above. But it must be noted, first, that the wave-length which should have been found is 74.5, a number differing but little from that actually found; second, that the waves were long and that the nodes were somewhat difficult to place exactly; and third, that the atomic weight of hydrogen has been taken as unity, whereas it is more likely to be 1.01, if oxygen, as was done, be taken as 16. The atomic weight 1.01 raises the found value of the ratio to 1.399, a number differing but little from the mean value found by other observers.

Having thus established the trustworthiness of the method, we proceed to describe our experiments with argon.

Five series of measurements were made with the sample of gas of density 19.82. It will be remembered that a previous determination with the same gas gave as its density 19.90. The mean of these two numbers was therefore taken as correct, viz., 19.86.

The individual measurements are:

<table>
<thead>
<tr>
<th>1.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>Mean.</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.16</td>
<td>18.14</td>
<td>18.02</td>
<td>18.04</td>
<td>18.03</td>
<td>18.08</td>
</tr>
</tbody>
</table>

millims.

for the half-wave-length. Calculating the ratio of the specific heats, the number 1.644 is obtained.

The narrowness of the tube employed in these experiments might perhaps raise a doubt regarding the accuracy of the measurements, for it is conceivable that in so narrow a tube the viscosity of the gas might affect the results. We therefore repeated the experiments, using a tube of 8 millims. internal diameter.

The mean of eleven readings with air, at 18°, gave a half-wave-length of 34.62 millims. With argon in the same tube, and at the same temperature, the half-wave-length was, as a mean of six concordant readings, 31.64 millims. The density of this sample of argon, which had been transferred from a water gas-holder to a mercury gas-holder, was 19.82; and there is some reason to suspect the presence of a trace of air, for it had been standing for some time.

The result, however, substantially proves that the ratio previously found was
correct. In the wide tube, \( C_p : C_v : 1.61 : 1 \). Hence the conclusion must be accepted that the ratio of specific heats is practically 1.66 : 1.

It will be noticed that this is the theoretical ratio for a monatomic gas, that is, a gas in which all energy imparted to it at constant volume is expended in effecting translational motion. The only other gas of which the ratio of specific heats has been found to fulfil this condition is mercury at a high temperature.\(^*\) The extreme importance of these observations will be discussed later.

15. Attempts to induce Chemical Combination.

A great number of attempts were made to induce chemical combination with the argon obtained by use of magnesium, but without any positive result. In such a case as this, however, it is necessary to chronicle negative results, if for no other reason but that of justifying its name, “argon.” These will be detailed in order.

(a) Oxygen in Presence of Caustic Alkali.—This need not be further discussed here; the method of preparing argon is based on its inactivity under such conditions.

(b) Hydrogen.—It has been mentioned that, in order to free argon from excess of oxygen, hydrogen was admitted, and sparks passed to cause combination of hydrogen and oxygen. Here again caustic alkali was present, and argon appeared to be unaffected.

A separate experiment was, however, made in absence of water, though no special pains was taken to dry the mixture of gases. The argon was admitted up to half an atmosphere pressure into a bulb, through whose sides passed platinum wires, carrying pointed poles of gas-carbon. Hydrogen was then admitted until atmospheric pressure had been attained. Sparks were then passed for four hours by means of a large induction coil, actuated by four storage cells. The gas was confined in a bulb closed by two stop-cocks, and a small V-tube with bulbs was interposed, to act as a gauge, so that if expansion or contraction had taken place, the escape or entry of gas would be observable. The apparatus, after the passage of sparks, was allowed to cool to the temperature of the atmosphere, and, on opening the stop-cock, the level of water in the V-tube remained unaltered. It may therefore be concluded that, in all probability, no combination has occurred; or, that if it has, it was attended with no change of volume.

(c) Chlorine.—Exactly similar experiments were performed with dry, and afterwards with moist, chlorine. The chlorine had been stored over strong sulphuric acid for the first experiment, and came in contact with dry argon. Three hours sparking produced no change of volume. A drop of water was admitted into the bulb. After four hours sparking, the volume of the gas, after cooling, was diminished by about

\( \frac{1}{6} \) cub. centim., due probably to the solution of a little chlorine in the small quantity of water present.

\( (d) \) Phosphorus.—A piece of combustion-tubing, closed at one end, containing at the closed end a small piece of phosphorus, was sealed to the mercury reservoir containing argon; connected to the same reservoir was a mercury gauge and a Sprengel’s pump. After removing all air from the tubes, argon was admitted to a pressure of 600 millims. The middle portion of the combustion-tube was then heated to bright redness, and the phosphorus was distilled slowly from back to front, so that its vapour should come into contact with argon at a red heat. When the gas was hot, the level of the gauge altered; but, on cooling, it returned to its original level, showing that no contraction had taken place. The experiment was repeated several times, the phosphorus being distilled through the red-hot tube from open to closed end, and vice versa. In each case, on cooling, no change of pressure was remarked. Hence it may be concluded that phosphorus at a red-heat is without action on argon. It may be remarked parenthetically that no gaseous compound of phosphorus is known, which does not possess a volume different from the sum of those of its constituents. That no solid compound was formed is sufficiently proved by the absence of contraction. The phosphorus was largely converted into the red modification during the experiment.

\( (e) \) Sulphur.—An exactly similar experiment was performed with sulphur, again with negative results. It may therefore be concluded that sulphur and argon are without action on each other at a red heat. And again, no gaseous compound of sulphur is known in which the volume of the compound is equal to the sum of those of its constituents.

\( (f) \) Tellurium.—As this element has a great tendency to unite with heavy metals, it was thought worth while to try its action. In this, and in the experiments to be described, a different form was given to the apparatus. The gas was circulated over the reagent employed, a tube containing it being placed in the circuit. The gas was dried by passage over soda-lime and phosphoric anhydride; it then passed over the tellurium or other reagent, then through drying tubes, and then back to the gas-holder. That combination did not occur was shown by the unchanged volume of gas in the gas-holder; and it was possible, by means of the graduated cylinder which admitted water to the gas-holder, to judge of as small an absorption as half a cubic centimeter. The tellurium distilled readily in the gas, giving the usual yellow vapours; and it condensed, quite unchanged, as a black sublimate. The volume of the gas, when all was cold, was unaltered.

\( (g) \) Sodium.—A piece of sodium, weighing about half a gramme, was heated in argon. It attacked the glass of the combustion tube, which it blackened, owing to liberation of silicon; but it distilled over in drops into the cold part of the tube. Again no change of volume occurred, nor was the surface of the distilled sodium tarnished; it was brilliant, as it is when sodium is distilled in vacuo. It may probably also be
concluded from this experiment that silicon, even while being liberated, is without action on argon.

The action of compounds was then tried; those chosen were such as lead to oxides or sulphides. Inasmuch as the platinum-metals, which are among the most inert of elements, are attacked by fused caustic soda, its action was investigated.

(h) Fused and Red-hot Caustic Soda.—The soda was prepared from sodium, in an iron boat, by adding drops of water cautiously to a lump of the metal. When action had ceased, the soda was melted, and the boat introduced into a piece of combustion-tube placed in the circuit. After three hours circulation no contraction had occurred. Hence caustic soda has no action on argon.

(i) Soda-lime at a red-heat.—Thinking that the want of porosity of fused caustic soda might have hindered absorption, a precisely similar experiment was carried out with soda-lime, a mixture which can be heated to bright redness without fusion. Again no result took place after three hours heating.

(j) Fused Potassium Nitrate was tried under the impression that oxygen plus a base might act where oxygen alone failed. The nitrate was fused, and kept at a bright red heat for two hours, but again without any diminution in volume of the argon.

(k) Sodium Peroxide.—Yet another attempt was made to induce combination with oxygen and a base, by heating sodium peroxide to redness in a current of argon for over an hour, but also without effect. It is to be noticed that metals of the platinum group would have entered into combination under such treatment.

(l) Persulphides of Sodium and Calcium.—Soda-lime was heated to redness in an open crucible, and some sulphur was added to the red-hot mass, the lid of the crucible being then put on. Combination ensued, with formation of polysulphides of sodium and calcium. This product was heated to redness for three hours in a brisk current of argon, again with negative result. Again, metals of the platinum group would have combined under such treatment.

(m) Some argon was shaken in a tube with nitro-hydrochloric acid. On addition of potash, so as to neutralise the acid, and to absorb the free chlorine and nitrosyl chloride, the volume of the gas was barely altered. The slight alteration was evidently due to solubility in the aqueous liquid, and it may be concluded that no chemical action took place.

(n) Bromine-water was also without effect. The bromine vapour was removed with potash.

(o) A mixture of potassium permanganate and hydrochloric acid, involving the presence of nascent chlorine, had no action, for on absorbing chlorine by means of potash, no alteration in volume had occurred.

(p) Argon is not absorbed by platinum black. A current was passed over a pure specimen of this substance; as usual, however, it contained occluded oxygen. There was no absorption in the cold. At 100°, no action took place; and on heating to MDCCCXCV.—A.
redness, by which the black was changed to sponge, still no evidence of absorption was noticed. In all these experiments, absorption of half a cubic centimetre of argon could have at once been detected.

We do not claim to have exhausted the possible reagents. But this much is certain, that the gas deserves the name "argon," for it is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character, ranging from sodium and magnesium on the one hand, to oxygen, chlorine, and sulphur on the other. It will be interesting to see if fluorine also is without action, but for the present that experiment must be postponed, on account of difficulties of manipulation.

It will also be necessary to try whether the inability of argon to combine at ordinary or at high temperatures is due to the instability of its possible compounds, except when cold. Mercury vapour at 800° would present a similar instance of passive behaviour.

16. General Conclusions.

It remains, finally, to discuss the probable nature of the gas or gases which we have succeeded in separating from atmospheric air, and which has been provisionally named argon.

That argon is present in the atmosphere, and is not manufactured during the process of separation is amply proved by many lines of evidence. First, atmospheric nitrogen has a high density, while chemical nitrogen is lighter. That chemical nitrogen is a uniform substance is proved by the identity of properties of samples prepared by several different processes, and from several different compounds. It follows, therefore, that the cause of the high density of atmospheric nitrogen is due to the admixture with heavier gas. If that gas possesses the density of 20 compared with hydrogen as unity, atmospheric nitrogen should contain of it approximately 1 per cent. This is found to be the case, for on causing the nitrogen of the atmosphere to combine with oxygen in presence of alkali, the residue amounted to about 1 per cent.; and on removing nitrogen with magnesium the result is similar.

Second: This gas has been concentrated in the atmosphere by diffusion. It is true that it cannot be freed from oxygen and nitrogen by diffusion, but the process of diffusion increases relatively to nitrogen the amount of argon in that portion which does not pass through the porous walls. That this is the case is proved by the increase of density of that mixture of argon and nitrogen.

Third: On removing nitrogen from "atmospheric nitrogen" by means of magnesium, the density of the residue increases proportionately to the concentration of the heavier constituent.

Fourth: As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen should, after removal of the oxygen, exceed that of "atmospheric nitrogen." Experiment has shown that the density is considerably increased.
A NEW CONSTITUENT OF THE ATMOSPHERE.

Fifth: It is in the highest degree improbable that two processes, so different from each other, should each manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from "atmospheric nitrogen."

Sixth: If the newly discovered gas were not in the atmosphere, the discrepancies in the density of "chemical" and "atmospheric" nitrogen would remain unexplained.

Seventh: It has been shown that pure nitrogen, prepared from its compounds, leaves a negligible residue when caused to enter into combination with oxygen or with magnesium.

There are other lines of argument which suggest themselves; but we think that it will be acknowledged that those given above are sufficient to establish the existence of argon in the atmosphere.

It is practically certain that the argon prepared by means of electric sparking with oxygen is identical with argon prepared by means of magnesium. The samples have in common:—

First: Spectra which have been found by Mr. Crookes, Professor Schuster, and ourselves to be practically identical.

Second: They have approximately the same density. The density of argon, prepared by means of magnesium, was 19.9; that of argon, from sparking with oxygen, about 19.7; these numbers are practically identical.

Third: Their solubility in water is the same.

That argon is an element, or a mixture of elements, may be inferred from the observations of § 14. For Clausius has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then

\[
\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v},
\]

\(C_p\) and \(C_v\) denoting as usual the specific heat at constant pressure and at constant volume respectively. Hence, if, as for mercury vapour and for argon (§ 14), the ratio of specific heats \(C_p : C_v\) be \(1\frac{3}{3}\), it follows that \(K = H\), or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of interatomic energy is regarded as proof of the monatomic character of the vapour, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion improbable in itself and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence it follows that argon is not of a compound nature.

According to Avogadro, equal volumes of gases at the same temperature and pressure, contain equal numbers of molecules. The molecule of hydrogen gas, the density of which is taken as unity, is supposed to consist of two atoms. Its mole-
molecular weight is therefore 2. Argon is approximately 20 times as heavy as hydrogen, that is, its molecular weight is 20 times as great as that of hydrogen, or 40. But its molecule is monatomic, hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of the elements in that mixture, taken for the proportion in which they are present, must be 40.

This conclusion rests on the assumption that all the molecules of argon are monatomic. The result of the first experiment is, however, so nearly that required by theory, that there is room for only a small number of molecules of a different character. A study of the expansion of argon by heat is proposed, and would doubtless throw light upon this question.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling, that in our future experimental work we shall endeavour to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have, therefore, to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one, or more than one, of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between 19, that of fluorine, and 23, that of sodium. But this view is apparently put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near 40 are:—

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>35.5</td>
</tr>
<tr>
<td>Potassium</td>
<td>39.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>40.0</td>
</tr>
<tr>
<td>Scandium</td>
<td>44.0</td>
</tr>
</tbody>
</table>

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming 37 (the
approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and 40 the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, 80, and rubidium, 85.5, viz., 82, the mixture should consist of 93.3 per cent. of the lighter, and 6.7 per cent. of the heavier element. But it appears improbable that such a high percentage as 6.7 of a heavier element should have escaped detection during liquefaction.

If the atomic weight of the lighter element were 38, instead of 37, however, the proportion of heavier element would be considerably reduced. Still, it is difficult to account for its not having been detected, if present.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains

$$S^4_{IV}, P^3_{IIII}, S^4_{VI}, \text{ and } Cl^3_{VIII},$$

might be expected to end with an element of monatomic molecules, of no valency, i.e., incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be perhaps excused, if they in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kellas, and Matthews, and especially to Mr. Percy Williams, for their assistance in the prosecution of this research.

**Addendum (by Professor W. Ramsay).**

March 20, 1895.

Further determinations of the density of argon prepared by means of magnesium have been made. In each case the argon was circulated over magnesium for at least
The general mean is 19'900; or if Nos. (2) and (3) be rejected as suspiciously low, the mean of the remaining four determinations is 19'941. The molecular weight may therefore be taken as 39'9 without appreciable error.

The value of R in the gas-equation R = pv/T has also been determined between — 89° and + 248°. For this purpose, a gas-thermometer was filled with argon, and a direct comparison was made with a similar thermometer filled with hydrogen.

The method of using such a hydrogen-thermometer has already been described by Ramsay and Shields.* For the lowest temperature, the thermometer bulbs were immersed in boiling nitrous oxide; for atmospheric temperature, in running water; for temperatures near 100° in steam, and for the remaining temperatures, in the vapours of chlorobenzene, aniline, and quinolene.

The results are collected in the following tables:—

**Hydrogen Thermometer.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (millims)</th>
<th>Volume (corr.)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>13'04</td>
<td>763-6</td>
<td>1'00036</td>
<td>2'6705</td>
</tr>
<tr>
<td>99'84</td>
<td>992-6</td>
<td>1'00280</td>
<td>2'6697</td>
</tr>
<tr>
<td>130'62</td>
<td>1073-8</td>
<td>1'00364</td>
<td>2'6701</td>
</tr>
<tr>
<td>185'36</td>
<td>1218-5</td>
<td>1'00618</td>
<td>2'6716</td>
</tr>
<tr>
<td>248'66</td>
<td>1351</td>
<td>1'00766</td>
<td>2'6737</td>
</tr>
<tr>
<td>— 87'92</td>
<td>497-3</td>
<td>0'99786</td>
<td>2'6804</td>
</tr>
</tbody>
</table>

* 'Trans. Chem. Soc.,' vol. 63, pp. 835, 836. It is to be noticed that the value of R is not involved in using the hydrogen-thermometer; its constancy alone is postulated.
A NEW CONSTITUENT OF THE ATMOSPHERE.

The value of $R$ is thus practically constant, and this affords a proof that the four last temperatures have been estimated with considerable accuracy.

**Argon Thermometer.**

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>°C.</td>
<td>millions.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series I</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 14²/5       | 701.7     | 1.000396       | 2.4446
| 14.27       | 689.7     | 1.000401       | 2.4366
| 14.40       | 702.6     | 1.000404       | 2.4462
| 99.96       | 906.5     | 1.00280        | 2.4379
| 160.00      | 904.8     | 1.00280        | 2.4322
| -87.92      | 455.6     | 0.99756        | 2.4556 |

By mischance, air leaked into the bulb; it was therefore refilled.

<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>°C.</td>
<td>millions.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series II</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 130.58      | 1060.0    | 1.00037        | 2.6363
| 135.46      | 1200.3    | 1.00052        | 2.6317

A bubble of argon leaked into the bulb, and the value of $R$ increased.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>°C.</td>
<td>millions.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series III</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 12.05       | 760.9     | 1.000344       | 2.6098
| 12.61       | 761.3     | 1.000344       | 2.6728
| 248.66      | 1384.0    | 1.0070         | 2.6717
| 248.66      | 1376.8    | 1.0070         | 2.6580
| -87.92      | 495.7     | 0.99756        | 2.6718

It may be concluded from these numbers, that argon undergoes no molecular change between $-88^\circ$ and $+250^\circ$.

Further determinations of the wave-length of sound in argon have been made, the wider tube having been used. In every case the argon was as carefully purified as possible. In experiment (3) too much lycopodium dust was present in the tube; that is perhaps the cause of the low result. For completeness' sake, the original result in the narrow tube has also been given.

<table>
<thead>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In air.</td>
<td>In argon.</td>
<td>Air.</td>
</tr>
<tr>
<td>Dec. 6</td>
<td>19.92</td>
<td>19.59</td>
<td>18.08</td>
<td>17.5</td>
</tr>
<tr>
<td>Feb. 15</td>
<td>19.96</td>
<td>33.73</td>
<td>31.00</td>
<td>6.7</td>
</tr>
<tr>
<td>Jan. 20</td>
<td>19.97</td>
<td>34.10</td>
<td>31.31</td>
<td>7.22</td>
</tr>
<tr>
<td>Mar. 19</td>
<td>19.94</td>
<td>34.23</td>
<td>31.68</td>
<td>11.20</td>
</tr>
</tbody>
</table>

The general mean of these numbers is 1.643; if (3) be rejected, it is 1.648. In the last experiment every precaution was taken. The half-wave-length in air is the mean of 11 readings, the highest of which was 34.67 and the lowest 34.00. They run:—
With argon the mean is also that of 11 readings, of which the highest is 31.83, and the lowest, 31.5. They are:

31.5; 31.5; 31.66; 31.55; 31.83; 31.77; 31.81; 31.83; 31.83; 31.50; 31.66.
11.8°; 11.8°; 11.20°; 11.40°; 11.60°; 11.40°; 11.40°; 11.5°; 11.5°; 11.4°.

If the atomic weight of argon is identical with its molecular weight, it must closely approximate to 39.9. But if there were some molecules of $A_2$ present, mixed with a much larger number of molecules of $A_1$, then the atomic weight would be correspondingly reduced. Taking an imaginary case, the question may be put:—What percentage of molecules of $A_2$ would raise the density of $A_1$ from 19.0 to 19.9? A density of 19.0 would imply an atomic weight of 38.0, and argon would fall into the gap between chlorine and potassium. Calculation shows that in 10,000 molecules, 474 molecules of $A_2$ would have this result, the remaining 9526 molecules being those of $A_1$.

Now if molecules of $A_2$ be present, it is reasonable to suppose that their number would be increased by lowering the temperature, and diminished by heating the gas. A larger change of density should ensue on lowering than on raising the temperature, however, as on the above supposition, there is not a large proportion of molecules of $A_2$ present.

But it must be acknowledged that the constancy of the found value of $R$ is not favourable to this supposition.

A similar calculation is possible for the ratio of specific heats. Assuming the gas to contain 5 per cent. of molecules of $A_2$, and 95 per cent. of molecules of $A_1$ the value of $\gamma$, the ratio of specific heats, would be 1.648. All that can be said on this point is, that the found ratio approximates to this number; but whether the results are to be trusted to indicate a unit in the second decimal appears to me doubtful.

The question must therefore for the present remain open.

Addendum.

April 9.

It appears worth while to chronicle an experiment of which an accident prevented the completion. It may be legitimately asked, Does magnesium not absorb any argon, or any part of what we term argon? To decide this question, about 500 grms. of magnesium nitride, mixed with metallic magnesium which had remained unacted on, during extraction of nitrogen from "air-nitrogen," was placed in a flask, to which a reservoir full of dilute hydrochloric acid was connected. The
flask was coupled with a tube full of red-hot copper oxide, intended to oxidise the hydrogen which would be evolved by the action of the hydrochloric acid on the metallic magnesium. To the end of the copper-oxide tube a gas-holder was attached, so as to collect any evolved gas; and the system was attached to a vacuum-pump, in order to exhaust the apparatus before commencing the experiment, as well as to collect all gas which should be evolved, and remain in the flask.

On admitting hydrochloric acid to the flask of magnesium nitride a violent reaction took place, and fumes of ammonium chloride passed into the tube of copper oxide. These gave, of course, free nitrogen. This had not been foreseen; it would have been well to retain these fumes by plugs of glass-wool. The result of the experiment was that about 200 cub. centims. of gas were collected. After sparking with oxygen in presence of caustic soda, the volume was reduced to 3 cub. centims. of a gas which appeared to be argon.
VII. On the Spectra of Argon.

By William Crookes, F.R.S., &c.

Received January 26.—Read January 31, 1895.

[Plate 3.]

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train. The results are both interesting and important, and entirely corroborate the conclusions arrived at by the discoverers of argon.

The results of my examination are given in a table of wave-lengths, which follows, and on a map of the lines accurately drawn to scale, accompanying this paper (Plate 3). The map is 40 feet long, and the probable error of position of any line on it is not greater than 1 millimetre.

Argon resembles nitrogen in that it gives two distinct spectra according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, both the argon spectra consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and, however free it was supposed to be from nitrogen, I could always at first detect the nitrogen bands in its spectrum. These, however, disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end. I have also used a Plücker tube made entirely of quartz worked before the oxy-hydrogen blow-pipe. I have not yet succeeded in melting platinum or iridio-platinum wire terminals into the quartz, as they melt too easily, but a very good spectrum is obtained by coating the bulbs outside with tin foil, connected with the terminals of the induction coil.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 millims. At this point the colour of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696·56 and 705·64. On passing the current the traces of nitrogen bands disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical
evaporation," and I think the residual nitrogen is occluded by the finely-divided metal. Similar occlusions are frequently noticed by those who work much with vacuum-tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. The two spectra, called for brevity red and blue, are shown on the large map, the upper spectrum being that of "blue" argon, and the lower one that of "red" argon. It is not easy to obtain the blue colour and spectrum entirely free from the red. The red is easily got by using a large coil actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue. The blue colour may be obtained with the same coil by actuating it with a current of 3.84 ampères and 11 volts, intercalating a jar of 50 square inches surface; the make-and-break must be screwed up so as to vibrate as rapidly as possible. With the small coil a very good blue colour can be obtained by using three Grove's cells and a Leyden jar of 120 square inches surface, and a very rapid make-and-break. It appears that an electromotive force of 27,600 volts is required to bring out the red, and a higher E.M.F. and a very hot spark for the blue. It is possible so to adjust the pressure of gas in the tube that a very slight alteration of the strength of the current will cause the colour to change from red to blue, and vice versa. I have occasionally had an argon tube in so sensitive a state, that with the commutator turned one way the colour was red, and the other way blue. Induction coils actuated by a continuous current are never symmetrical as regards the polarity of the induced current, and any little irregularity in the metallic terminals of the vacuum-tube also acts as a valve. The red glow is produced by the positive spark and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.† In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all. Of these 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay, I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, con-

---

† The coil used has about 60 miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove's cells.
‡ Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.
taminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour’s current and a few days’ rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is submitted to the induced current in a tube made of fused and blown quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum-tube was filled with argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 amperes and 11 volts, no jar being interposed. At a pressure of 3 millims. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until, at a pressure of about half a millimetre, flashes of blue light made their appearance. At a quarter of a millimetre the colour of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

A striking instance of a change of spectrum from nitrogen to argon was shown in a tube filled with argon kindly sent me by Lord Rayleigh. It had been prepared from the atmosphere by sparking, and it was considered to contain about 3 per cent. of nitrogen. This argon was passed into an exhausted tube and then rarefied to a pressure of 75 millims. and kept on the pump. At this pressure the nitrogen conducted all the induction current, the spectrum showing nothing but the nitrogen bands. The pump was slowly kept going and spectrum observations were continuously taken. When the pressure fell to about 3 millims. a change came over the spectrum, the nitrogen bands disappeared, and the spectrum of argon took its place, the only contamination being a little aqueous vapour, due to my not having sufficiently dried the gas. I took photographs of the spectrum given by this tube in the two stages, one showing the pure nitrogen bands and the other the argon lines, each being compared with the spectrum of argon prepared by Professor Ramsay. Observations have shown that the spectra given by argon, obtained by the sparking method of Lord Rayleigh and by the magnesium method of Professor Ramsay from the atmosphere, are identical.

It was of interest to see how little argon could be detected in admixture with nitrogen by combined pumping and passage of the current. Some argon prepared by myself,* having 60 to 70 per cent. of nitrogen with it, was put into a small tube furnished with large platinum terminals. Exhaustion was carried to 3 millims., and

* When a current of 65 volts and 15 amperes, alternating 130 times a second, is passed through the primary of my large coil, an arching flame, consisting of burning nitrogen, issues from each of the secondary poles, meeting in the middle. When once started, the poles can be drawn asunder till the flame bridges across 212 millims. When the terminals are more than 46 millims. apart, the flame will not strike across. By enclosing this flame in a reservoir over alkaline water and feeding it with air and oxygen I can burn up a litre of air an hour.
the tube was then sealed off. The spark from the large coil, actuated with a current of 3·84 amperes and 11 volts, was then put on, and the spectrum examined continuously. At first it showed only the nitrogen bands; in about half an hour the nitrogen began to fade and the argon lines appeared, and in a few minutes later the tube was just short of non-conducting. The colour of the gas was rich steel blue, and the spectrum was that of the blue argon glow. Here the small diameter of the bulbs of the tube and the large platinum wires facilitated much spattering or "electrical evaporation" of the platinum; the pressure also was the one most suitable for that phenomenon. To this I attribute the rapid occlusion of the residual nitrogen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 millims. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time I used it for photographing the nitrogen spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The colour immediately changed from the reddish-yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty, and by employing a very small jar, I was able to take one photograph of this changed spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through except by employing a dangerously large current. Whenever a flash passed it was of a deep blue colour. Assuming that the atmosphere contains 1 per cent. of argon, the 3 millims. of nitrogen originally in the tube would contain 0·03 millim. of argon. After the nitrogen had been occluded by the spattered platinum this pressure of argon would be near the point of non-conduction.

In all cases, when argon has been obtained in this manner, the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark; partly also on the degree of exhaustion. Nitrogen, when present, conducts the current easiest. As the exhaustion increases and the conductivity of the nitrogen diminishes, that of the red-glowing argon rises, until, at a pressure of about 3 millims., its conductivity is at the greatest, and the luminosity is best. Beyond that point the conductivity of the red form seems to get less, and that of the blue form to increase, till the vacuum approaches a fraction of a millimetre, when further pumping soon renders it non-conducting. It is not improbable, and I understand that independent
observations have already led both the discoverers to the same conclusion, that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen, which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

The disappearance of the red glow and the appearance of the blue glow in argon as the exhaustion increases also resembles the disappearance of the red line of hydrogen when exhaustion is raised to a high point. Plücker, who was the first to observe this occurrence, says: "When Ruhmkorff's small induction coil was discharged through a spectral tube enclosing hydrogen, which was gradually rarefied to the highest tenacity to be reached by means of Geissler's exhauster, finally the beautiful red colour of the ignited gas became fainter, and passed gradually into an undetermined violet. When analysed by the prism, Hα (the red, C, line) disappeared, while Hβ (the green, F, line), though fainter, remained well defined. Accordingly, light of a greater length of wave was the first extinguished."

The line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed shows that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at 581·7, the aurora line at 557·1, and the helium line at 587·5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapour yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. Having once obtained a tube of argon giving the pure spectra, I can make no alteration in it, except that which takes place on varying the spark or increasing the exhaustion, when the two spectra change from one to the other. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.


The Two Spectra of Argon.

<table>
<thead>
<tr>
<th>Wave-length.</th>
<th>Intensity</th>
<th>Wave-length.</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td></td>
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119 lines in the "Blue" Spectrum.
80 lines in the "Red" Spectrum.
199 total lines.
26 lines common to the two spectra.

**Note.**—In the spectroscope the lines of argon appear almost equally fine, but of very different intensities. This difference of brightness is represented in the accompanying map by a variation in the thickness of the lines, faint lines being made narrow and strongly luminous lines being widened. In some cases two or three strong lines are too close together to enable their intensities to be represented in this way without overlapping. This is the case with lines 442.65 and 442.25, with lines 420.10, 419.80, and 419.15, and with lines 415.95 and 415.65. In these cases I have indicated the centres of the strong lines by short projecting lines beneath.
THE SPECTRA OF ARGON.
VIII. The Liquefaction and Solidification of Argon.

By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

Communicated by Professor William Ramsay, F.R.S.

Received January 28,—Read January 31, 1895.

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behaviour at low temperatures and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 cub. centims. It was contained in a hermetically-sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully-dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19·9 (H = 1); and he thought that at the outside it might contain 1 to 2 per cent. of nitrogen, although it showed no nitrogen spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as of measuring its vapour pressure at several other low temperatures, while two other series served to determine its boiling- and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding 1 millim.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both
ends with glass stop-cocks. By connecting the lower end of the burette with a mercury reservoir, the argon was transferred into a narrow doubly bent glass tube connected with the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

**Determination of the Critical Constants of Argon.**

As soon as the temperature of the liquid ethylene had been lowered to $-128^\circ{\text{C}}$, the argon easily condensed to a colourless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:
In all seven determinations the critical pressure was found to be 50·6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapour pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature. This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is —121°, and this may be taken as the critical temperature of argon.

At lower temperatures the following vapour-pressures were recorded:

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<td>38·0</td>
<td>13</td>
<td>—134·4</td>
<td>29·8</td>
</tr>
<tr>
<td>9</td>
<td>—129·6</td>
<td>33·8</td>
<td>14</td>
<td>—135·1</td>
<td>28·0</td>
</tr>
<tr>
<td>10</td>
<td>—129·4</td>
<td>35·8</td>
<td>15</td>
<td>—136·2</td>
<td>27·3</td>
</tr>
<tr>
<td>11</td>
<td>—129·3</td>
<td>35·8</td>
<td>16</td>
<td>—138·3</td>
<td>25·3</td>
</tr>
<tr>
<td>12</td>
<td>—129·6</td>
<td>35·8</td>
<td>17</td>
<td>—139·1</td>
<td>23·7</td>
</tr>
</tbody>
</table>

In Experiments Nos. 9, 10, and 17 the quantity of liquefied argon was very small, for it filled the tube only to a height of 3 to 5 millims., and in the other experiments the column of liquid argon was 20 millims. or more.

**Determination of the Boiling- and Freezing-Points.**

Two hundred cub. centims. of liquid oxygen, prepared in my large apparatus,* was poured into a glass vessel with quadruple walls, so as to isolate the liquid from

---

* *Bulletin International de l'Académie de Cracovie,' June, 1890; also Wiedemann's 'Beiblätter,' vol. 15, p. 29.
external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 cub. centims., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature (−182°7) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by increasing the atmospheric pressure by a quarter. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below −187°, the liquefaction of the argon became manifest. When liquefaction had taken place, I carefully equalised the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers: −186°7, −186°8, −187°0, and −187°3. The mean is −186°9, which I consider to be the boiling-point under atmospheric pressure (740·5 millims.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 99·5 cub. centims.; the quantity of liquid corresponding to that volume of gas was approximately 0·114 cub. centim. Hence the density of argon at its boiling-point may be taken as approximately 1·5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point (−187°) is much higher than that of oxygen, which I have found, under similar conditions, to be 1·124.

By lowering the temperature of the oxygen to −191° by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers: −189°0, −190°6, −189°6, and −189°4. The mean of these numbers is −189°6; and this may be accepted as the melting-point of argon.

In the following table I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

---

* I have re-determined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1°3 lower than that which I previously recorded.
LIQUEFACTION AND SOLIDIFICATION OF ARGON.

<table>
<thead>
<tr>
<th>Name</th>
<th>Critical temperature</th>
<th>Critical pressure</th>
<th>Boiling point</th>
<th>Freezing point</th>
<th>Freezing pressure</th>
<th>Density of gas</th>
<th>Density of liquid at boiling point</th>
<th>Colour of liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>Below -320-0</td>
<td>Atmos. 20-0</td>
<td>°</td>
<td>°</td>
<td>10</td>
<td>0-885</td>
<td>Colourless</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>-146-0</td>
<td>35-5</td>
<td>-194-4</td>
<td>-214-0</td>
<td>60</td>
<td>14-0</td>
<td>0-885</td>
<td></td>
</tr>
<tr>
<td>Carbonic oxide (CO)</td>
<td>-139-5</td>
<td>35-5</td>
<td>-190-0</td>
<td>-207-0</td>
<td>100</td>
<td>14-0</td>
<td>0-885</td>
<td></td>
</tr>
<tr>
<td>Argon (A)</td>
<td>-121-0</td>
<td>50-6</td>
<td>-187-0</td>
<td>-189-6</td>
<td>?</td>
<td>19-9</td>
<td>Colourless</td>
<td></td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>-118-8</td>
<td>50-8</td>
<td>-182-7</td>
<td>?</td>
<td>16-0</td>
<td>1-124</td>
<td>Bluish</td>
<td></td>
</tr>
<tr>
<td>Nitric oxide (NO)</td>
<td>-93-5</td>
<td>71-2</td>
<td>-133-6</td>
<td>-167-0</td>
<td>138</td>
<td>15-0</td>
<td>?</td>
<td>Colourless</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>-81-8</td>
<td>54-9</td>
<td>-164-0</td>
<td>-185-8</td>
<td>80</td>
<td>8-0</td>
<td>0-415</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from the foregoing table, argon belongs to the so-called “permanent” gases, and, as regards difficulty in liquefying it, it occupies the fourth place, viz., between carbon monoxide and oxygen. Its behaviour on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its simple molecular constitution.

NOTE ON A COMPARISON OF THE VAPOUR-PRESSURES OF ARGON WITH THOSE OF OTHER SUBSTANCES.

By William Ramsay and Sydney Young.

Received February 7, 1895.

The vapour-pressures of a considerable number of substances have been determined from low temperatures to the critical points, but as the critical pressure of argon is somewhat high, the boiling-points of very few are available for comparison through the whole range of equal pressures.

The critical pressure of benzene is so slightly below that of argon that the extrapolation of the vapour-pressure curve through the few degrees necessary to afford a comparison at the critical pressure of the new element is justifiable.

The other two substances chosen are ethyl alcohol and oxygen; the second is interesting, as its vapour-pressures, like those of argon, have been determined by Professor Olszewski.

In the following table the boiling-points—on the absolute scale—of argon, benzene, MDCCCXCV.—A.
PROFESSOR K. OLSZEWSKI ON THE

ethyl alcohol, and oxygen, are given at the pressures at which observations have been made with the first of these substances.

**Boiling-Points on Absolute Scale.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>740.5</td>
<td>86.1</td>
<td>352.5</td>
<td>350.5</td>
<td>90.1</td>
</tr>
<tr>
<td>18010</td>
<td>133.9</td>
<td>507.8</td>
<td>462.6</td>
<td>136.1</td>
</tr>
<tr>
<td>19230</td>
<td>134.7</td>
<td>512.5</td>
<td>465.8</td>
<td>137.4</td>
</tr>
<tr>
<td>20750</td>
<td>136.8</td>
<td>518.0</td>
<td>468.6</td>
<td>139.0</td>
</tr>
<tr>
<td>22040</td>
<td>137.9</td>
<td>522.3</td>
<td>472.7</td>
<td>140.2</td>
</tr>
<tr>
<td>22650</td>
<td>138.6</td>
<td>524.3</td>
<td>474.0</td>
<td>141.4</td>
</tr>
<tr>
<td>27210</td>
<td>143.5</td>
<td>533.3</td>
<td>483.7</td>
<td>145.0</td>
</tr>
<tr>
<td>28850</td>
<td>144.4</td>
<td>543.9</td>
<td>487.0</td>
<td>145.5</td>
</tr>
<tr>
<td>38460</td>
<td>152.0</td>
<td>565.9</td>
<td>503.1</td>
<td>153.7</td>
</tr>
</tbody>
</table>

The ratios of the absolute temperatures of argon to each of the other substances were calculated and plotted against the centigrade temperatures of the latter. Straight lines were then drawn to pass as well as possible through the points, and the following formulae for the ratios were obtained:—

\[
R' = -2351 + 0.001155 t \quad (t = \text{temperature centigrade of benzene}).
\]

\[
R' = -2164 + 0.0003765 t \quad (t = \text{temperature centigrade of ethyl alcohol}).
\]

\[
R' = 9518 + 0.00522(t+190) \quad (t = \text{temperature centigrade of oxygen}).
\]

The ratios calculated from the boiling-points and those given by the above formulae are compared in the following table:—

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From boiling-points.</td>
<td>From formula.</td>
<td>From boiling-points.</td>
</tr>
<tr>
<td>740.5</td>
<td>2443</td>
<td>2443</td>
<td>2455</td>
</tr>
<tr>
<td>18010</td>
<td>2637</td>
<td>2642</td>
<td>2694</td>
</tr>
<tr>
<td>19230</td>
<td>2648</td>
<td>2628</td>
<td>2892</td>
</tr>
<tr>
<td>20750</td>
<td>2641</td>
<td>2634</td>
<td>2913</td>
</tr>
<tr>
<td>22040</td>
<td>2640</td>
<td>2639</td>
<td>2917</td>
</tr>
<tr>
<td>22650</td>
<td>2644</td>
<td>2641</td>
<td>2924</td>
</tr>
<tr>
<td>27210</td>
<td>2696</td>
<td>2657</td>
<td>2967</td>
</tr>
<tr>
<td>28880</td>
<td>2659</td>
<td>2663</td>
<td>2965</td>
</tr>
<tr>
<td>38460</td>
<td>2686</td>
<td>2689</td>
<td>3021</td>
</tr>
</tbody>
</table>
LIQUEFACTION AND SOLIDIFICATION OF ARGON.

Assuming the boiling-points of benzene, alcohol, and oxygen to be correct, those of argon could be calculated from them by multiplying the absolute temperatures of each substance by the corresponding ratio at each pressure.

The observed and re-calculated absolute temperatures of argon and the differences are given below:

<table>
<thead>
<tr>
<th>Pressure in millims.</th>
<th>Boiling-points (absolute) of argon.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed.</td>
</tr>
<tr>
<td>740.5</td>
<td>86.1</td>
</tr>
<tr>
<td>18010</td>
<td>133.9</td>
</tr>
<tr>
<td>19230</td>
<td>134.7</td>
</tr>
<tr>
<td>20750</td>
<td>136.8</td>
</tr>
<tr>
<td>22040</td>
<td>137.9</td>
</tr>
<tr>
<td>22650</td>
<td>138.6</td>
</tr>
<tr>
<td>27210</td>
<td>143.3</td>
</tr>
<tr>
<td>28880</td>
<td>144.4</td>
</tr>
<tr>
<td>38460</td>
<td>152.0</td>
</tr>
</tbody>
</table>

The comparison would, of course, be more valuable if there were some observations between 740 and 18,000 millims., but, so far as it goes, it will be seen that there is a very fair agreement between the observed temperatures and those calculated from the smoothed ratios.

It is hardly likely, though not impossible, that so good an agreement would be obtained with a mixture or an impure substance. It is, at any rate, certain that a distinct want of agreement would have shown that the argon was not a definite, pure substance, and the results may be taken as affording additional confirmation of the conclusion that argon is a definite, hitherto unknown constituent of the atmosphere, and that it has been isolated in a state very closely approaching to purity.
IX. The Latent Heat of Evaporation of Water.


Communicated by R. T. Glazebrook, F.R.S.

Received December 28, 1894,—Read January 17, 1895.

[Plates 4—6.]

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Section I.—Introductory Note.

It is possible that I have in succeeding pages, when describing apparatus and methods of observation, entered unnecessarily into matters of detail. In defence,
I would urge that the accuracy of determinations of physical constants depends on the amount of attention devoted to apparently trivial matters, and that in the absence of full information, it is impossible to rightly estimate the value of the results. Corrections are often rendered necessary by subsequent re-determinations of the constants involved, and the application of such corrections is only possible when the writer has given his data in full. Much valuable experimental work has with lapse of time become useless, owing to the author's natural reluctance to over-crowd his communication with details which may at the time very possibly appear both unnecessary and trivial.

Although the experiments described in this paper were not commenced until the Summer of last year (1894), the preparation of the apparatus and the standardisation of the instruments has engaged my attention for a considerable time. Nearly the whole of the Spring and Summer of 1893 were expended in fruitless efforts to render the calorimeter and its connections absolutely air-tight, and I found it impossible to secure perfection in this respect until in the Autumn of that year I succeeded in obtaining an alloy, by means of which I was able to unite glass and metal tubes in a satisfactory manner. The calorimeter and connections had then to be practically reconstructed and some improvements added, which experience had shown to be desirable.

My original intention was to conclude my investigations into the latent heat of evaporation of water over the range 10° to 60° C. before publishing my results, and, had it not been for two misfortunes, I think that I should have now completed the necessary experiments. An accident to the apparatus early in September involved a loss of about ten days, and also compelled a re-determination of the capacity for heat of the calorimeter. A second mischance was a temporary break-down in my health, which compelled me to be absent from my laboratory for some days, and on resuming the work I was at first able to devote but little energy to it. During the University Term my time is not my own, and hence, when October 13 found the inquiry unfinished, I was compelled to relinquish all hopes of completing my original scheme until the Long Vacation of 1895 should again provide me with the necessary leisure.

I feel, however, that all the experimental difficulties have been overcome, and I regard the work as completed at certain temperatures. I do not propose to repeat the observations at those temperatures, and therefore I see no necessity to defer the publication of the results for another twelve months.

Again, the facts set forth in Section XI. appear to me to so strengthen the conclusions to which my experiments have led me as to render any postponement unnecessary.

I wish to express my sincere thanks to Mr. C. T. Heycock and Mr. F. H. Neville for many valuable suggestions, and also for their help with the experiments on certain critical occasions.
HEAT OF EVAPORATION OF WATER.

During the summer of 1893 I was assisted by Mr. G. M. Clark, B.A., and throughout 1894 by Mr. C. Green, Scholar of Sidney Sussex College, and I am glad to have this opportunity of acknowledging my indebtedness to both those gentlemen.

As frequent references have to be given to two former papers, I denote them as follows:—


Section II.—Historical.

The following is, I think, a fairly complete table of results published since the year 1843:—

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Observer</th>
<th>No. of experiments</th>
<th>Extreme values for L.</th>
<th>Mean L.†</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>Dieterici</td>
<td>20</td>
<td>395.52-598.84</td>
<td>596.8</td>
<td>'Wied. Ann.,' vol. 37, 1889</td>
</tr>
<tr>
<td>-2° to 16°</td>
<td>Regnault</td>
<td>22</td>
<td>..</td>
<td>..</td>
<td>'Mémoir. de l'Acad.,' vol. 21, 1847</td>
</tr>
<tr>
<td>63°-88°</td>
<td>..</td>
<td>23</td>
<td>533.3-538.4</td>
<td>536.67</td>
<td>..</td>
</tr>
<tr>
<td>99°-81°</td>
<td>Favre and Silbermann</td>
<td>3</td>
<td>532.59-541.77</td>
<td>535.77</td>
<td>'Ann. de Chimin.,' vol. 37, 1853</td>
</tr>
<tr>
<td>100°</td>
<td>Andrews</td>
<td>8</td>
<td>530.8-543.4</td>
<td>535.9</td>
<td>'Chem. Soc. Journ.,' 1849</td>
</tr>
<tr>
<td>100°</td>
<td>Berthelot</td>
<td>3</td>
<td>535.2-537.2</td>
<td>536.2</td>
<td>'Comptes Rendus,' vol. 5, 1877</td>
</tr>
<tr>
<td>100°</td>
<td>Schall</td>
<td>No details given</td>
<td>532.0</td>
<td></td>
<td>'Ber. d. Chem. Ges.,' vol. 17, 1884</td>
</tr>
<tr>
<td>100°-16°</td>
<td>Hartog and Harker</td>
<td>5</td>
<td>523.61-525.87</td>
<td>524.60</td>
<td>'Manchester Phil. Soc. Proc.,' 1893-4</td>
</tr>
<tr>
<td>119°-194°</td>
<td>Regnaut</td>
<td>73</td>
<td>..</td>
<td>..</td>
<td>'Mémor. de l'Acad.,' vol. 21, 1847</td>
</tr>
</tbody>
</table>

The values obtained by Winkelman ('Wied. Ann.,' vol. 9, 1880) are not included in the above table, as they are not based on independent experiments, but deduced from the observations of Regnaut.

I do not propose to examine at length any of the above determinations except those

* It is right to add that Messrs. Hartog and Harker state that these are the results of "Preliminary Experiments," and should not be regarded as giving their final conclusions. I do not, therefore, include their work in my criticisms.

† It must be remembered that all the above values of L (with the exception of Dieterici's) depend upon some assumption as to the changes in the specific heat of water caused by changes in temperature, for they are either deduced from "the total heat of steam," or depend upon the observation of the rise or fall in temperature of a certain mass of water. Again, as the nature of the thermal unit adopted by the observer is, in some cases, doubtful, an uncertainty of an order of about 1 per cent. is thus introduced.
by Regnault and Dieterici, for none of the other observers appear to me to have devoted as much care and attention to the matter. In some cases, e.g., Andrews and Berthelot, we have records of only a few observations evidently undertaken not so much with the object of obtaining an accurate determination of the latent heat of evaporation of water, but rather for purposes of comparison with other liquids. In other cases there are not sufficient details as to the thermometry, the unit of heat adopted, &c., to render a close criticism of any profit.

Again, Dieterici is the only observer who has made direct experiments at temperature 0° C. Regnault's observations extended from 63° to nearly 200° C., and he also performed a number of experiments where the temperature of the vapour was between — 2° and + 16°, although this last group must be regarded (and I think was regarded by Regnault himself) as of less value than his observations at higher temperatures.

The method employed by Dieterici was in principle very similar to that adopted by me and described in subsequent pages.*

The heat required for the evaporation was abstracted from water at 0° and the amount of heat deduced from the quantity of ice formed. The advantages of such a method (upon which I shall more fully dwell when I describe my own work) are as follows:

(1.) No change of temperature takes place, thus all difficulties connected with the capacity for heat of the apparatus and its contents are avoided.

(2.) The observer is almost entirely independent of thermometry—an advantage which, to my mind, it is almost impossible to overestimate.

Dieterici's experimental results, as stated in Table I. (supra), vary from 595.52 to 598.84, but it should be noticed that both these extremes occur in his Table I. He afterwards made what he considered to be improvements in the apparatus, and the extreme values of his last 13 experiments (see his Tables II., III., IV.) are 595.74 and 597.29. His mean result is 596.80, and I would particularly draw attention to his last two experiments, where he very greatly increased the rapidity of evaporation by suddenly opening the communication between his evaporating vessel and a condenser containing sulphuric acid in which the pressure was reduced as far as possible by means of a mercury pump. These two experiments give respectively 597.07 and 596.68. The agreement between the individual experiments throughout the whole series leaves little to be desired, and, if it were not for one doubt, I would without hesitation accept those results as conclusive; but I am afraid, for the following reasons, that our knowledge is not yet sufficiently exact.

The quantities of heat were deduced by measuring the mass of mercury expelled from the Bunsen calorimeter during the formation of ice, and the results, therefore,

* My own experiments described in this paper were completed before the work of Dieterici came to my notice, and the close similarity between the general principles adopted by both of us is a matter of chance, not of design. Had I previously perused his paper, I should have been saved much time and many preliminary experiments.
HEAT OF EVAPORATION OF WATER.

265
depend entirely on the constant which gives the relation between the quantity of heat and the mass of expelled mercury. **Dieterici** in this matter shifts the responsibility on to other shoulders. His only reference to the subject is as follows:—

"Diese sind gemessen in mittleren Calorien, also in dem hundertsten Theile derjenigen Warmemenge, welche ein Gramm Wasser von 0° auf 100° erwärmt, und zwar liegt der Berechnung der Mittelwerth der Beobachtungen von Bunsen, Schuller und Wartha und Velten,* zu Grunde dass einer mittleren Calorie 15'44 mg. Hg. entsprechen."†

Now, **Bunsen** by assuming his own value of this constant obtained 80'025 as the latent heat of fusion of ice, and the marked difference between this number and that obtained by **Regnault** (79'24), requires explanation. This discrepancy is greater than appears at first sight, for the "mean thermal unit" (over the range 100° to 0°) adopted by **Bunsen** is supposed to be greater than the "thermal unit at 15°" adopted by **Regnault** during his researches into Latent Heat, and thus the divergence would be increased if both were expressed in terms of the same thermal unit.

The doubt introduced by the above considerations is due to uncertainty regarding the comparative magnitude of the different thermal units and does not affect the value of **Dieterici**'s experiments, although it renders his conclusions somewhat uncertain.

There can be but little doubt that the mass of mercury expelled from a Bunsen calorimeter by the subtraction of a definite thermal unit is a quantity that can be, and doubtless will be, determined with accuracy, and if any correction on the conclusions arrived at by **Bunsen**, **Schuller** and **Wartha**, and **Velten** is found to be necessary, it can be applied to the values of the latent heat of evaporation at 0° obtained by **Dieterici**.

This case well illustrates a matter to which I have before endeavoured to call attention,† viz., that a mistake in thermometry is a fatal error in experimental work. It is impossible to correct the conclusions arrived at by the investigator, however our knowledge of thermometry may increase, since we should require to have in our possession the actual thermometer used by the observer, together with a full knowledge of the circumstances under which it was observed. As before remarked, **Dieterici**'s results were independent of thermometry, hence their peculiar value.

**Regnault**'s formula for the "total heat of steam" has been so generally accepted, and the experiments upon which he founded it are so justly considered as examples of that singular skill and ability for which all his work is distinguished, that it is with diffidence that I venture to offer criticisms on his methods or conclusions. I would repeat that **Regnault** himself evidently attached less importance to his determina-

* The actual values obtained by these observers were as follows:—**Bunsen**, 15'41; **Schuller** and **Wartha**, 15'44; **Velten**, 15'47 mg. 'Wied. Ann.,' vol. 33, 1888, p. 439.
‡ 'Science Progress,' April, 1894.
tions at low temperatures than to those above 65°C. In Table IV. of his paper, "Sur les chaleurs latentes de la vapeur aqueuse à saturation sous diverses pressions," are given the results of all his experiments below 65°, and in his introductory remarks to this table (pp. 712–719) he clearly indicates his comparative want of confidence in the results.\(^*\)

A searching criticism of Regnault's work is given by Winkelmann in 'Wied. Ann.,' vol. 9, 1880, and had the limits of this communication permitted it, I should have liked to quote several pages of that paper, but I will content myself with giving a short summary of his arguments.

I would first remark that Winkelmann's object was to explain the discrepancy between what he terms the "theoretical density" of water vapour, and that which results from "the mechanical theory of heat." He assumes the former as 0.6225; but does not give the data by which he obtains that number (I find that if we take the molecular weight of H\(_2\)O as 18.01, and the density of H as 0.6924 (air = 1), we arrive at the same value). He then (assuming that J = 424) calculates the density from the thermodynamic equation \(L = T/J (s' - s) dP/dT\), by substituting for \(L\)—

(a) the values resulting from Regnault's formula for the "total heat," viz.,

\[606.5 + 3054t,\]

(b) the values of \(L\) given by the equation

\[L = 589.5 - 0.2972t - 0.0032147t^3 + 0.000008147t^3. \ldots (W),\]

the last being a formula constructed by Winkelmann, but based on Regnault's experiments at high temperatures.

Winkelmann contends that not only does the use of (W) bring the values obtained by the "mechanical theory" into greater harmony with the "theoretical value," but also that the formula (W) is in closer agreement with Regnault's experiments than is the formula given by Regnault himself.

True, the values obtained by Winkelmann are always greater than 0.6225, but he contends that it is impossible to imagine the real density as less than the "theoretical," although it is easy to see that it may be greater.

---

\(^*\) "J'ai cherché à obtenir la chaleur latente de la vapeur d'eau à saturation aux basses températures par une autre méthode qui me permettra, j'espère, d'obtenir cette donnée avec beaucoup d'exactitude et contre laquelle on ne peut pas élever les objections que nous avons faites contre le premier procédé. Mais cette méthode, que j'ai décrite à la fin de mon Mémoire sur l'hygrométrie ('Annales de Chimie et de Physique,' 3\(^e\) série, tome 15, p. 227), exige la connaissance de plusieurs données sur lesquelles il reste encore beaucoup d'incertitude. On a besoin notamment de connaître la capacité calorifique de l'air et la quantité de chaleur que l'air absorbe pendant sa dilatation. Il m'a paru nécessaire de déterminer ces deux éléments par de nouvelles expériences, et c'est seulement lorsque celles-ci seront terminées que je pourrai calculer les déterminations de la chaleur latente de la vapeur d'eau," p. 722.
When I give the results of my experiments, I think that I shall be able to show that Winkelmann in his desire to lower the value of $L$ at low temperatures has considerably overshot the mark, and that in deducing the values at, or near, $0^\circ$ from experiments above $65^\circ$, he has carried the method of extrapolation beyond due bounds. At present, however, I will only consider his reasons, with which I agree in the main, for rejecting Regnault's determinations at lower temperatures.

(1) There is no doubt that Regnault's formula does not give the mean result of his experiments at low temperatures. In all, he performed twenty-two experiments at temperatures below $65^\circ$ (Table IV., 'Mémoire. de l'Acad.', xxi., 1847), and the mean value given by these twenty-two experiments differs from that given by his formula by 1:8.

(2) The experiments above referred to were performed in a different manner from those at the higher temperatures. The water to be evaporated was placed in a spiral within the calorimeter, and the pressure reduced until the water boiled, the vapour being condensed in a vessel surrounded by ice. Regnault deduced the temperature of the water when evaporating by observing the pressure of the vapour in the condenser—hence, as Regnault himself says, "It is probable that the elastic force observed on the barometric manometer is decidedly less than the mean pressure at which the vapour is distilled," and thus the evaporation is taking place under a greater pressure and at a higher temperature than that given by his Table IV.

Again, the temperature of the saturated vapour is sensibly beneath the temperature of the calorimeter, and so lowers the temperature of the calorimeter more than would be done by the evaporation alone.

In the case of other liquids, Regnault made a correction for the heat abstracted by the vapour while passing out of the calorimeter, but he did not apply this correction in the case of water. It is true that no special arrangements were made to warm the vapour to the calorimetric temperature (as was done by coils with the vapours of other liquids), but there can be no doubt that the vapour must have abstracted heat from the walls of the calorimeter.

Let $k$ be the specific heat of the vapour, $t$ the temperature at which evaporation takes place, $t_0$ and $t_1$ the initial and final temperatures of the calorimeter, then the heat per unit mass absorbed should be $k \{ \frac{1}{2} (t_0 + t_1) - t \};$ at the same time this is not a correction that can be applied with certainty.

(3) At these low temperatures a small difference in the pressure of the vapour corresponds to a considerable difference in temperature; thus, if the temperature of the water is deduced from the pressure in the receiver, the error may be considerable.* The effect of all these errors would be to make the value of $L$ given by Regnault's experiments too great.

The above criticisms do not apply to the experiments at the higher temperatures.

* For example, a difference of 0:4 millim. at $4^\circ$ would correspond to a difference of 1° C.
I think the preceding summary fairly represents the remarks of Winkelmann on the determinations at low temperatures. *

I will now add some remarks of my own.

Regnault was compelled to limit the duration of these experiments as much as possible, otherwise his correction for the loss or gain by radiation, etc. (which was at best but a somewhat uncertain one) became large as compared with the other magnitudes to be measured. The average length of an experiment was about five minutes, though in one or two extreme cases it extended to 11 minutes; in this time he evaporated about 5.3 grams of water, and thus he was compelled to reduce the pressure in the condenser very considerably below the pressure of saturated vapour at the temperature of the calorimeter. He was, therefore, unable to diminish the sources of error (subsequently dwelt upon by Winkelmann) in the manner he might have done had he not been thus limited in time. Regnault, referring to the difference between the pressure in the condenser and in the calorimeter, writes as follows: "La différence entre les deux tensions doit même être assez grande; car pour que l'expérience se fasse dans des conditions favorables d'exactitude; il faut que la distillation soit assez rapide, afin que la correction e ne soit jamais qu'une fraction très-petite de $t_0 - t_1$."

Again, another matter of importance is the thermometry. On p. 692 (ibïd.) he says: "Les thermomètres à mercure des calorimètres ont été gradués avec le plus grand soin, un degré centigrade occupe sur la tige du thermomètre

\[
\text{du calorimètre C. . . . . 18°7620; par suite 1° vaut 0°053283.}
\]
\[
\text{,, C'. . . . . 18°5800; ,, 1° ,, 0°053821.}
\]

Il est facile d'apprécier avec certitude le dixième des divisions, c'est-à-dire $\frac{1}{100}$ de degré centigrade dans les lunettes horizontales avec lesquelles on observe les thermomètres."

The only other reference is on p. 707, where he remarks that he reduced the readings from the mercury to the air scale by means of the table given on p. 239 of his paper "De la mesure des Températures."† I have searched the paper throughout for some indication as to the thermometers actually used, in the hope that I might be able to identify them with some one of those of whose comparison with the air thermometer he gave an account in another paper; but the above are the only references to the thermometry that I have been able to find. Had a direct comparison between these thermometers and the air thermometer been made, it is most probable that Regnault would have mentioned it; we may, therefore, assume that,

* Had not Regnault measured the temperature of the evaporating water by means of the vapour pressure in the condenser, the above objections would lose their force.
† 'Mémoir. de l'Acad.,' vol. 21, 1847, p. 716.
‡ 'Mémoir. de l'Institut,' vol. 21, p. 220
knowing the nature of the glass, he simply reduced them to the air scale by the table above referred to.

Throughout the low temperature determinations the temperature of the calorimeter fell during an experiment through about $5^\circ6$ (in the greatest case $5^\circ761$), and thus an error of $0^\circ01$ in his thermometry would cause a difference of more than 1 in 600 in the results. At higher temperatures, however, the average rise in the temperature of the calorimeter exceeded $12^\circ$ and thus the effect of any such thermometric error would be considerably reduced.

Again, the observations of the change in temperature of the calorimeter at low temperatures were always taken on a falling thermometer. I have in a previous paper (J., p. 442) expressed my disbelief in the value of any observations of mercury thermometers when their temperature is falling: I am not alone in this opinion, and it has been confirmed by subsequent experience. I am sure that inaccuracies of a much larger order than $0^\circ01$ would have presented themselves from this cause alone, and the great divergences observable amongst Regnault's individual experiments at low temperatures is I have no doubt partly attributable to this cause.† In all his experiments at higher temperatures, however, his thermometers were rising and the discrepancies between individual observations were much less marked.

It will be noticed that the various sources of error which have been enumerated either disappear or are much diminished at the higher temperatures.

Again, the ever-recurring difficulty with regard to the specific heat of water presents itself. The correction is not so simple as has been assumed by those who have merely applied Regnault's own formula for the specific heat of water to the expression for the total heat of steam, for the correction would have to be applied during the reduction of each separate experiment, as the quantity of heat absorbed by the calorimeter and contents when warming or cooling through a degree of temperature would vary according to the mean temperature of the range and the resulting correction would, I believe, be greater than is usually supposed.

There appears to be but little doubt that Regnault's expression for the changes in the specific heat of water is inaccurate. As far as I know, Rowland (1877), Bartoli and Stracciati (1889), and myself (1892) are the only observers who have seriously attacked this difficulty since the time of Regnault, and all agree in one conclusion, viz., that the specific heat of water diminishes as the temperature rises to $20^\circ$, and the methods of experiment employed by these observers were so entirely different that their agreement in this matter carries great weight. We cannot, therefore, accept without question Regnault's conclusions as to the changes at higher temperatures. The magnitude of the correction involved may be illustrated, as pointed out by Dieterici himself, by the following example. If we assume

* Schuster and Gannon, Communication to the Royal Society, Nov. 22, 1894.
† The comparatively slow rate of stirring would also tend to make the temperature measurements uncertain.
Rowland's value for the specific heat of water at 15° C., the difference between the thermal unit at 15° C. and "the mean thermal unit" over the range 100° to 0°, amounts (if we accept Dieterici's interpretation of Regnault's values) to nearly 1½ per cent., and would reduce the value of L at 0°, as given by Regnault's formula (viz. 606.5), below the value found by Dieterici (598.8).†

The tacit assumption amongst physicists that the discrepancies arising from doubts as to the value of the thermal unit are so trivial that they may be disregarded is, as shown by the above example, much to be regretted, and the many efforts to deduce specific volumes, etc., from the equation \( J = \frac{L}{T}(s' - s) \frac{dp}{dT} \), shows how frequently this difficulty is ignored. It is strange that, although so much attention has been devoted, during recent years, to the exact determination of various physical units, so little has been done with regard to this extremely important fundamental constant.

The experimental difficulties are not so great as to prevent all progress, and I venture to appeal to the Royal Society to consider this matter; indeed, I would go so far as to express my personal belief that the method of measuring small differences of temperature indicated in a paper read before the Physical Society last October removes many of the difficulties which have hitherto barred the way.

It is, I think, evident that we are not justified in concluding that our knowledge of the value of the latent heat of evaporation of water at low temperatures is sufficient. It has been already shown that the effect of most of the causes of error above enumerated diminishes at higher temperatures; and a study of Regnault's Tables I. to III. will confirm the conclusion that we may regard the results at those temperatures as of greater accuracy. Even at higher temperatures, however, the difficulties with regard to the measurement of differences of temperature and of the capacity for heat of water present themselves.

I can find no record of experiments by any observer at temperatures between 16° and 65° C.

The above considerations are, I think, sufficient to indicate the necessity of a re-determination of the latent heat of evaporation of water, at all events at low temperatures.

Section III.—Description of the Method.

I was anxious, if possible, to devise a method of such a nature that my results would not be appreciably affected by

1. errors in thermometry,
2. changes in the specific heat of water,
3. the capacity for heat of the calorimeter,
4. loss or gain of heat by radiation, &c.,

* At the end of this paper I give figures which lead to the conclusion that the difference between the "mean thermal unit" and the "thermal unit at 15°" is less than is usually assumed.
and if these points are borne in mind they may serve to explain some of the contrivances which might otherwise appear uncalled for.

If the vessel in which the evaporation is taking place is kept at a constant temperature, we are independent of the capacity for heat of it and its contents; we also dispense with the measurements of changes of temperature. Thus, if matters be so arranged that the loss and gain of heat throughout an experiment are balanced, many fruitful causes of error are avoided. Of course, the actual temperature of the calorimeter during evaporation must be determined, but a small error here is of little consequence. The change in the value of $L$ (when $L$ is the latent heat of evaporation of water) is small as compared with the changes in $\theta$. In fact, an accuracy of an order of $\frac{1}{10}$ of a degree would be sufficient when determining the actual elevation.

The heat was supplied to the calorimeter by means of a wire whose ends were kept at a constant potential difference. The thermal balance could be maintained in one of two ways,

1. If the heat supply was too great, the electric current could be temporarily stopped: or, the rate of evaporation of the water increased. (The latter was the method that I generally adopted.)

2. If the cooling was too rapid, the only mode of maintaining the balance was (in the apparatus about to be described) to reduce the rate of evaporation.

The water to be evaporated was placed in a small silver flask, connected with which was a spiral coil of silver tubing 18 feet in length. Both flask and spiral were within the calorimeter, and the water-vapour, after passing through the spiral, emerged from the apparatus at the temperature of the calorimeter. Surrounding the flask, and between it and the spiral, a coil of platinum silver wire was arranged, and flask, spiral and coil were entirely immersed, in aniline during my preliminary experiments, subsequently in a certain oil of which an account will be given later.

The calorimeter (which was filled to the roof with the aniline or oil, and the equality of temperature maintained by rapid stirring) was suspended by glass tubes within a steel chamber, whose walls were maintained at a constant temperature. So long, therefore, as the calorimeter and the surrounding walls were at equal temperatures, there was no loss or gain by radiation, &c. If during an experiment the temperature of the surrounding walls changed, the method of experiment involved a corresponding change in the temperature of the calorimeter, and, therefore, some loss or gain of heat would be experienced. The apparatus was so designed that any such change in temperature was extremely small (in no case amounting to $\frac{1}{100}$), yet, in order to estimate the loss or gain, it was necessary to know approximately the capacity for heat of the calorimeter and contents.

Small differences between the temperature of the calorimeter and the surrounding walls would, during an experiment, be of no consequence, provided that the oscillations were of such a nature that the mean temperature of the calorimeter was that of the
surrounding space, and I think I shall be able to show that this condition was fulfilled.

In addition to the heat supplied by the electric current there is also a supply due to the work done by the stirrer. It was in the estimation of this "stirring supply" that I found my greatest difficulties, and I regard that portion of my determinations with the least confidence. Fortunately the heat thus generated was only about \( \frac{1}{100} \) of the heat supplied by the current, and thus any small error in that portion of the work becomes of little account.

Of the accuracy with which the electrical supply could be measured, there is no question, and I have but one remark to make on this portion of the subject, viz., that even if the values of the E.M.F. of my Clark cells, or the absolute resistance of the box-coils given by the standardisations performed during my determinations of J, are in any way inaccurate, such errors would eliminate, since the value of J was determined by means of the same standards as those by which the quantity of heat developed in these experiments was determined. Hence, by assuming my former value of J, I get the comparison in terms of a thermal unit at 15° C., independently of the numerical value of J assumed in the reductions.

One further correction remains to be noticed. I have spoken of the temperature of the calorimeter as oscillating about the exterior temperature, and it might happen that at the close of an experiment this difference was not the same as that at the commencement—if any such difference existed. The magnitude of this correction depended, of course, on the ability of the observer to maintain the thermal balance. In these experiments the correction was extremely small, and in any case could be determined with great accuracy.

Having indicated the nature of the observations I will proceed to state the relation between the various sources of loss, or gain of heat.

Let \( Q_e \) be the thermal units per second due to the electrical supply, \( Q_m \) mechanical supply, \( \Sigma q \) total heat supply during an experiment from any other causes.

Then, if M be the mass of water evaporated, L the latent heat of evaporation at temperature \( \theta \), and if the electrical supply is maintained for a time \( t_e \), and the mechanical for a time \( t_m \),

\[
ML = Q_e t_e + Q_m t_m + \Sigma q \tag{1}
\]

Now the D.P. at the ends of the coil was always some integral multiple of the D.P. of a Clark cell.

Let \( e \) be the D.P. of a Clark cell, \( n \) the number of cells, and \( R_1 \) the resistance of the coil at the temperature \( \theta_1 \), then

\[
Q_e = \frac{e^2 n^2}{R_1 J} \tag{2}
\]
HEAT OF EVAPORATION OF WATER.

If the calorimeter at the commencement and end of an experiment was at exactly the same temperature as the surrounding walls, then if their temperature was unchanged, the term $\Sigma q$ would vanish; but although this term throughout these experiments was of small dimensions, it could not be entirely ignored.

Let $\theta'_0$ and $\theta''_0$ be the temperature of the surrounding walls at the beginning and end of an experiment; suppose the calorimeter temperature ($\theta_1$) to exceed the surrounding temperature by $d'$ at the commencement and $d''$ at the end of an experiment. Then fall in temperature of calorimeter

$$= (\theta'_0 + d') - (\theta''_0 + d'').$$

Hence the heat given out by the calorimeter in consequence of this fall in temperature is

$$C_k \{ (\theta'_0 + d') - (\theta''_0 + d'') \},$$

where $C_k$ is the capacity for heat of calorimeter and contents at the temperature $\theta_1$.

If we neglect any small loss by radiation, &c., due to the differences $d'$ and $d''$ between the temperature of the calorimeter and the surrounding walls, we may conclude that the whole of the heat thus evolved by the calorimeter was expended in the evaporation of water, hence

$$\Sigma q = C_k \{ (\theta'_0 - \theta''_0) + (d' - d'') \} \tag{3}$$

Hence

$$ML = \frac{e^2 \mu^2 \times t_s}{R_j J} + Q_s \times t_s + C_k \{ (\theta'_0 - \theta''_0) + (d' - d'') \} \tag{4}$$

In order to convey an idea of the relative importance of the terms in equation (4) I will here give the approximate mean value of each term resulting from the experiments described in succeeding pages.

| Table II. |
|---|---|---|
| | $Q_s t_s$ | $Q_s \times t_s$ | $\Sigma q$. |
| When $\theta_1 = 40$ and $n = 4$ | 2150 | 19.2 | $\pm 1.6$ |
| $\theta_1 = 30$ and $n = 4$ | 2305 | 32.9 | $\pm 1.2$ |
| $\theta_1 = 30$ and $n = 3$ | 1752 | 32.9 | $\pm 1.2$ |

* This apparently clumsy method of representing the quantity of heat evolved or taken up by the calorimeter was adopted because, as the method of experiment involved separate determinations of $\theta'_0$, $\theta''_0$, $d'$ and $d''$, the actual temperature of the calorimeter at any time could only be obtained in this manner.

MDCCCXC.-A.
Although, of course, I had, when commencing these experiments, no exact knowledge as to the comparative values of the terms, some preliminary observations enabled me to form a rough estimation of their magnitudes and consequently of the degree of attention which should be devoted to their accurate measurement.

Section IV.—The Method of Maintaining the Space surrounding the Calorimeter at a Constant Temperature.

I have, in Paper J., given an account of the apparatus employed for this purpose, and full details and plates will be found on pp. 374–378 (ibid.).

In order, however, to give a general idea of the arrangements, and to save the reader the trouble of reference, I will here quote the brief description given in the abstract of that paper:—"The calorimeter was suspended within an air-tight steel chamber. The walls and floor of this chamber were double, and the space between them filled with mercury. The whole structure was placed in a tank containing about 20 gallons of water, and was supported in such a manner that there were about three inches of water both above and beneath it. The mercury was connected by a tube with a gas regulator of a novel form, which controlled the supply of gas to a large number of jets. Above these jets was placed a flat silver tube, through which tap-water was continually flowing into the tank, all parts of which were maintained at an equal temperature by the rapid rotation of a large screw. Thus, the calorimeter may be regarded as suspended within a chamber placed in the bulb of a large thermometer—the mercury in that bulb weighing 70 lbs. A change of 1° C. in the temperature of the tank-water caused the mercury in the tubes of the regulating apparatus to rise about 300 millims. Special arrangements were made by which it was possible to set the apparatus so that the walls surrounding the calorimeter could be maintained for any length of time at any required temperature, from that of the tap-water (in summer about 13° C., in winter 3° C.) up to 40° C. or 50° C."

I think the above summary, together with the section on Plate 4, will convey a sufficient idea of the apparatus.

Since 1892, I have made certain improvements, which I will briefly describe.

During my J. experiments the range of temperature was from about 14° C. to 26° C. In subsequent experiments when I have required to use the apparatus at higher temperatures, it was found that the oscillations in temperature became serious, in some cases amounting to \(\frac{1}{30}\)° C. This was due to the temperature lag of the large mass of mercury, so that when the gas was lowered by the action of the regulator the resulting in-flow of cold water lowered the tank temperature before the mercury had contracted sufficiently to again heat the in-flow. In Paper A. I have described as follows the arrangements made to meet this difficulty:—"As now arranged, when working above temperatures about 20° C., a small motor acts as a heart, and, the tap-water being shut off, pumps the tank-water itself round through the silver tube placed above the
gas-jets. The water, by passing through the pump, &c., is slightly cooled; thus, the work of the regulator is confined to simply supplying the heat lost by convection, radiation, &c., and it performs this task admirably. As an illustration, I may mention that, in the series of over 50 experiments treated of in this communication, on only one occasion did the temperature of the steel chamber change by as much as 1/100° C. throughout the duration of an experiment. On the solitary occasion that a change amounting to nearly 1/30° C. was observed, the cause was found in the caking of the lime through which the gas was passed on its way to the regulator, and, in consequence, the experiment was discarded before working out its results.”

On account of the use of the differential thermometers (see Section V.) employed in the present investigation, it was essential that any changes in the temperature of the steel chamber should be measured with greater accuracy than was necessary in my previous work, for now such changes influenced the temperature measurements, whereas on former occasions they only affected the loss by radiation, etc. An open range mercury thermometer placed in mercury in the hole E (Plate 4) gave the temperature of the walls surrounding the calorimeter and changes in the mean stem temperature had to be guarded against for the reason above given. The small motor already referred to now served another purpose. A portion of the water raised by the pump, instead of returning to the tank through the silver tube passed into a coil of about 20 feet of “compo.” tubing inserted in the tank, was then forced up a glass tube surrounding the stem of the thermometer, and passing out at the top, returned to the tank. Thus the stem-temperature was kept constant throughout an experiment, the regularity of the flow being secured by an overflow system. True, the water near the top of the glass tube would be slightly cooler than the tank water when working at high temperatures, but this was of no consequence, as the chief use of the thermometer was to detect differences during an experiment. Two thermometers labelled A and II. were used. Although an accuracy of an order of 1/10° C. would have been sufficient in actual elevation, I compared these thermometers every 0°-3 C. of their range with two different Tonnelot thermometers, standardised by the Bureau International des Poids et Mesures, and also with my own platinum standard. The results of the separate comparisons (expressed on the nitrogen scale) agreed within 0.005° C.

The stems of both thermometers were graduated in millimetres. A (range 16° to 26° C.) having about 27 millims. per 1° C. and II. (range 28° to 53° C.) about 20 millims. per 1° C. A table was constructed for the whole range of temperature, giving the value in degrees C. of (a) each millimetre of these thermometers in terms of the air thermometer, and (b) in terms of the millimetres of the “mean bridge wire scale” used by me for the determination of differences of temperature.

These thermometers were observed through a microscope fitted with a micrometer scale so divided that it gave 10 divisions to the millimetre. There was no difficulty
in estimating \( \frac{1}{10} \) of the micrometer divisions, and thus readings could be taken to
‘01 millim., that is to about ‘0004° C. on A and to about ‘0005° C. on No. II.

I do not, of course, claim that I could determine actual temperatures to this
cleneness, by these or any other mercury thermometers, but, owing to the precautions
above described, I have no doubt but that changes in temperature of the order of
0°001 C. (i.e., about ‘025 millim.) could be detected, especially as any movement was
extremely slow—in no case as much as 0°01 C. per hour. A constant vibration,
due to the pumping of the water up the surrounding tube, tended to prevent
“sticking.”

A further improvement has been the addition of a gas pressure regulator. This
apparatus was designed for me by Mr. Horace Darwin, and is the only satisfactory
instrument of the kind I have seen. It is most perfect in its action, and I am now
absolutely indifferent to changes of pressure in the mains.

With these additions, I think that the whole of this constant temperature portion
of the apparatus may be considered as nearly perfect. Only those who have watched
it actually at work can appreciate the certainty of its action; it can be set with
precision to any temperature between that of the tap-water and 64° (the highest
temperature at which I have actually tested it), and my only regret is that cir-
cumstances compel me to leave unused, for the greater portion of each year,
apparatus by means of which so many difficulties could be overcome.

Section V.—Description of the Calorimeter and its Connections.

The calorimeter was made of brass and was of cylindrical form, 10 centims. in
diameter and 10 centims. in height.

It contained a silver flask, F (see Plate 5, fig. 1), in which the evaporation took
place; a stirrer, of which the lower end only is shown at S; a rack (shown in the
horizontal section, Plate 5, fig. 2) which carried a coil of platinum-silver wire, and
about 18 feet of silver tubing wound in a spiral—shown in section at p.p'. A
platinum thermometer also passed from the top to the bottom. With so many
objects crowded into so small a space, it is difficult to convey any clear idea of the
internal arrangements, therefore I will only attempt a brief description, and shall
rely chiefly on the sections given in Plate 5 to convey the necessary information.
The capacity of the flask, F, up to the side opening at \( d \), was about 68 cub. centims.
Any vapour or gas passing from the flask into the spiral at \( d \), after descending to the
bottom of the calorimeter, ascended throughout the whole length of the coil, and
therefore the tube e. This arrangement was adopted to diminish any chance of the
carrying of the liquid, or “priming,” by the flow of vapour or gas, as it appeared
improbable that particles of liquid would be carried up a gentle slope of 18 feet in
length.
Any inflow of gas came down the tube \( f \), and passed directly into the bottom of the flask at \( g \).

The stirrer \( S \) had two paddles, reaching from top to bottom of the flask; the blades and the central tube were of thin copper. Down this tube passed a steel shaft, which hung at the lower extremity within a hole in a sheet of brass projecting from the side of the calorimeter. The bearings of the stirrer were entirely outside the calorimeter, and the lower end did not touch the base, or bear on the surrounding plate, whose only purpose was to check vibration. The paddles had a slight “pitch,” so as to throw the liquid upwards, as well as cause it to rotate. The exterior bearings at the top of the glass tube \( S \) (fig. 3) were of the kind figured in Plate 2, Paper J., and were certainly sufficiently air-tight to prevent any diffusion, even when the stirrer was rotating rapidly, but, as the calorimeter was filled with a non-volatile liquid, the air-tightness of this joint was of little consequence, especially as the temperature of the calorimeter remained constant during the experiments and the air-space above the liquid was small. The rubbing surfaces were very true and always immersed in oil, thus the heat generated must in any case have been unimportant. The greater portion of any heat developed in the external bearings would pass to the brass tube, of which they formed a part, and, as the lower portion of this tube was washed by the tank water, its temperature would in any case rise but little. Any heat passing down the steel shaft (length 28 centims., diameter 0·35 centim.) would, of course, be included in the “stirring correction,” but I should imagine that it was in reality negligible, for about 4 inches of the glass tube down which it passed were also washed by the tank water.

Further, slightly above the top of the calorimeter a section of ivory was inserted in the stirring shaft, in order to diminish conduction as much as possible.

The platinum-silver coil was wound on small ebonite tubes surrounding the narrow brass pillars of the rack, whose section is shown at \( R \) (fig. 2). The method by which the insulation of the rack was maintained, where the two brass pillars \( R_1 \) \( R_2 \) passed through the top of the calorimeter, is shown by the section (Plate 5, fig. 4). It must be remembered that these junctions had not only to be perfectly insulated, but that they had also to be absolutely air-tight, over a considerable range of temperature \( (10^\circ \text{ to } 60^\circ \text{ C.})^* \) even to pressures of 1 atmosphere.

The platinum-silver coil was about 100 centims. in length, and so wound that it was completely immersed when the depth of the liquid was 4 centims. Two copper wires (B.W.G., 21) were soldered to each of the pillars \( R_1 \) \( R_2 \) where they projected above the roof of the calorimeter at \( l \) and \( l' \) (fig. 3), thus, in the steel lid, there were four junctions similar to those above described (see Plate 6, fig. 3). The blocks of ebonite forming the top slab of the junctions were, however, in this case, made nearly five inches in length; they projected as far as the lid of the tank, and

* The insulation of the whole circuit after all the apparatus was placed in position, was better than 1 could measure, \( i.e., 10^7 \) ohms.
thus all contact between the leads and tank-water was prevented. The calorimeter was hung below the steel lid by five glass tubes, thus ten air-tight junctions of glass to metal were required, in fact, four of these junctions were, in reality, double ones, for the lower extremities of the narrow tubes c and f (Plate 5, fig. 1) had not only to be fixed into the lid of the calorimeter, but also joined on to the ends of the silver tubing. In like manner, where they passed through the steel lid, they had to join also on to glass tubes leading to two glass taps immersed in the outer tank. There were, therefore, practically fourteen such joints. I have previously described an alloy by which I was enabled to make these joints absolutely air-tight.* In order to show how carefully all these joints were tested, as well as several others in the external connections by which communication with the mercury pumps was established, I extract the following from Paper A. :—"In the spring of this year the intra-mural space was exhausted until the reading of the McLeod gauge connected therewith was reduced to 11, indicating a pressure of about 0.12 millim. The apparatus was then left untouched for a month, except that the temperature was occasionally raised or lowered, and at the end of that time the reading of the gauge was still less than 12. Dry air was then re-admitted to this space, and the silver flask, with its connecting tubes (embracing about 50 feet of tubing with several joins), tested in a similar manner. Those who have had to deal with low pressures will understand that, when all was found satisfactory, a great difficulty had been surmounted. I did not retain this vacuum during the experiments, as I felt that it would subject the glass tubes, &c., to a continuous strain which the conditions of the experiments rendered unnecessary. The labour had not been lost, however, for I was able to count with confidence on the gas-tightness of the whole apparatus."

Where the supporting glass tubes entered the calorimeter lid (as shown by the plan, Plate 5, fig. 3), they were surrounded by metal tubes (shown by the outer ring in each case) nearly 1 centim., in length which had their lower extremities soldered to the lid. The annular space between these and the glass tubes was filled with the alloy and the joints on the top of the steel lid, from which the apparatus hung, were of the same kind but slightly deeper. The tube S surrounded the stirrer shaft. The platinum thermometer AB passed down T, and this tube was also used for inserting or withdrawing the calorimeter liquid. The thermometer was wrapped with indiarubber tape so that the annular space between it and the glass tube T was made air-tight throughout the upper 4 inches.

Through h', h communication was established between the exterior and the silver flask. During my earlier experiments a thermometer stood in this tube with its bulb nearly at the bottom of the flask. It was of course possible to render air-tight the connection between the thermometer stem and the top of the tube h', where the latter projected above the tank. This would not, however, have been sufficient, for the flask contained a volatile liquid, and distillation would

have taken place into and out of the annular space between the tube and thermometer stem, according as the calorimeter was warmer or cooler than the tank water. This thermometer had also to be frequently removed in order to insert liquids into the flask, and therefore any junction at the bottom could not be made a permanent one. The difficulty was surmounted as follows:--The silver tube $k$ (Plate 5, fig. 1), which passed up from the lid of the silver flask was soldered to the calorimeter lid, above which it projected. A hollow brass rod just fitting the glass tube, but with its lower end tapered, was, before fixing the glass in place, held vertically with the tapering end filling the open end of the silver tube. The annular space between the silver and surrounding brass tube was then filled with the melted alloy, to above the top of the silver, and the glass tube lowered into its final position. When the alloy hardened, the brass rod was loosened by lowering into it a red-hot wire. The lower inch or so of the brass rod having been cut off was then placed co-axially round the thermometer stem and made one with it by filling the annular space between it and the stem with the same invaluable alloy. Thus, on lowering the thermometer into its place, the brass tube almost exactly fitted into the ring of alloy at the bottom of the glass tube. The fit was made good by prolonged grinding with rotten stone—using the thermometer stem as a rotating shaft. The result was a practically air-tight join at the calorimeter lid. It must be remembered that as the air-tightness was secured by the cork at the upper end, this joint had not to stand any pressure, but was only required to prevent diffusion.

I have, for two reasons, fully described this method of fixing the tube. (1) I thereby overcame a difficulty which had perplexed me for a long time; (2) it was necessary to explain the constriction at the lower end of the tube $h$, which in its turn became a source of difficulty when I altered my method of experiment.

$l$ and $l_1$ (fig. 3) are the insulating junctions for the rack on which the coil was wound.

The base of the calorimeter, which was not fixed until everything else was in place, was heated until solder contained in the circular trough, of which a section is shown at M (fig. 1), became fluid; the calorimeter was then pressed down upon it, and, as soon as the solder commenced to harden, the calorimeter was set in cold water. The base was thus soldered on without melting the alloy in the lid or injuring the internal fittings.

The whole apparatus was a difficult and complicated one to construct, and I owe my sincere thanks to Mr. Thomas for the ingenuity and patience he devoted to the task. My brief description can convey but little idea of the many difficulties that had to be surmounted between the conception and completion of this apparatus, and I may mention that although commenced in February, 1893, it was not until the spring of this year (1894) that the calorimeter could be regarded as completed.
Exterior Connections.

The upper end of the narrow glass entrance tube $f$ (Plate 5, fig. 1) was, as before stated, connected with a glass single-way tap $T_3$ (Plate 6, fig. 1), which, on the further side was connected with about 30 feet of thin-walled copper tubing immersed in the tank water. Thus, all gas entering the silver flask through $T_3$ would be at the temperature of the tank water, and (the calorimeter temperature being identical with that of the tank) no heat would be added or subtracted when gas was passed through the flask and spiral. $T_4$ was a four-way tap on the exit side, the arms of the one passage through its core being at right angles to each other. The tap is shown in fig. 1 (infra). $A$ is the tube leading from the flask and connected with $e$ (Plate 5, fig. 1). By rotating the core, $A$ could be connected with $B$ or $D$, or $C$ could be connected with $B$ or $D$. The glass tubes forming the outer case of both taps $T_3$ and $T_4$ were sealed at the lower extremity, and after a portion of the tube above the core had been filled with mercury, these taps were perfectly air-tight. The outer glass tube of each was about 6 inches long; thus the lower 4 inches were below the surface of the tank water, and the upper parts of the tubes were packed with cotton wool. The cores narrowed to a glass rod, which, passing through the wool, projected above the tank lid, where a handle was attached; thus the taps could be opened or shut from the exterior of the whole apparatus. The position of the taps is indicated in Plate 6, fig. 1.

Tube $B$ (fig. infra) which communicated with the apparatus into which, during my earlier experiments, the vapour was passed, extended under the surface of the water to the walls of the tank, it then passed above a row of small gas jets, and thus no condensation took place until the vapour arrived at the drying bulbs. At the close of an experiment a movement of the tap connected $C$ and $B$, and as $C$ was connected by a three-way tap ($T_2$, Plate 6, fig. 1) with the dry air supply, any moist air remaining in $B$ or its continuation was swept into the receiving apparatus. On the other hand, by connecting $A$ and $D$ before the commencement of an experiment the vapour brought by the gas which had passed through the calorimeter was disposed of without affecting the weight of the receiving apparatus attached to $B$. Thus an experiment could be started at any moment by changing the connection at tap $T_4$ from $AD$ to $AB$, and that without altering in any way the conditions as to flow of gas, rate of evaporation, &c.

Finally, I would remark that throughout the gas circuit, the gas only came into contact with the following materials—glass, silver (only hard solder was used for all the flask and tube connections), the glass-metal-joining alloy at the junctions, and the drying agents. True, in my “exhaust” experiments with water the vapour had to pass through about half-an-inch of thick rubber on the exit side, where connection was made with the condenser, but when using other liquids, this joint can easily be replaced by a glass one. When evaporating ether (with which I have made some
preliminary experiments), the grease on the cores of the glass taps was replaced by a trace of phosphoric acid, which appeared to answer admirably. Thus, the apparatus can be used without alteration for all volatile liquids which do not act on the metals, a possibility I kept steadily in view when designing it.

Fig. 1.

Four way tap $T_4$

[May 4, 1895.—At the meeting of the Physical Society on January 11, 1895, Professor Ramsay exhibited an apparatus by means of which the comparative latent heats of evaporation of different liquids could be determined. I had the pleasure of seeing the apparatus at work, and from that time I abandoned all idea of extending my own investigation to other liquids than water. The method adopted by Professor Ramsay is so perfect, and at the same time so simple, that I feel that it would be waste of time and energy to pursue my absolute determinations. I mention this because many of the precautions described in the preceding sections were adopted with the view of conducting experiments with various liquids, and (as I now discover) might have been dispensed with.

Professor Ramsay now informs me that, although certain practical difficulties in the working of his apparatus have not as yet been entirely overcome, he has already determined (approximately) the comparative latent heats of evaporation of a considerable number of volatile compounds, and that the results will shortly be published.

I venture, however, to call attention to the fact that the very perfection of Professor Ramsay’s method increases the importance of an accurate knowledge of the absolute latent heat of evaporation of water.]
Section VI.—The Determination of $\Sigma q$.

I will now describe the method of obtaining the value of the various terms in Equation I. (p. 272) by which the quantity of heat supplied during an experiment is ascertained.

$\Sigma q$ is the quantity whose accurate determination presented the greatest difficulty, therefore the apparatus was so designed as to reduce this term to as small dimensions as possible, and since many of the contrivances adapted to this end may, unless their purpose is explained, appear unnecessary and cumbersome, I commence with this term in order to avoid repetitions.

Had it been possible to so arrange matters that the temperature of the calorimeter at the beginning and end of an experiment should be absolutely unaltered, this term ($\Sigma q$) would have vanished, and in my earlier experiments, during which I endeavoured to determine the mass of water evaporated by passing the resulting vapour through drying bulbs, this condition was practically fulfilled, since it was always possible to stop an experiment at any time. I was compelled, for reasons which will be given later, to abandon this method of estimating $M$, and to adopt a method in which a given mass of water was to be evaporated. The observer had, therefore, no choice as to the time when the experiment should be completed, and as the thermal balance could not be absolutely maintained throughout an experiment, it was impossible to ensure the identity of the initial and final temperatures.

It was advisable, if possible, to so arrange matters (I.) that a small alteration in the quantity of heat should produce a considerable change in temperature, so that small differences in the thermal equilibrium might render themselves evident; (II.) that the oscillation in temperature might be reduced to as small dimensions as possible; (III.) that the difference, if any, between the initial and the final temperatures should be accurately measured.

Although Nos. I. and II. appear contradictory, such is not the case, for the important matter was to ensure the equality of the thermal, as distinct from the temperature balance; therefore, if small alterations in the former made themselves readily evident by changes in the latter, and if the latter changes were kept small, the desired end was attained.

Within the calorimeter there were two agencies at work—the cooling due to the evaporation (which for convenience I shall henceforth venture to speak of as a "supply of cold"), and a supply of heat due to the current; therefore, unless some means were adopted of rapidly bringing the contents to a uniform temperature, the temperature gradient from the hotter to the colder portions would be considerable. It was thus necessary to completely fill the calorimeter with some liquid and to rapidly stir this liquid.

Two objections to the use of water immediately presented themselves: (a) its great capacity for heat (which would have caused changes in the thermal balance to have
but a small effect on the temperature); (b) its electric conductivity, which would have necessitated the covering of the platinum-silver coil with some insulator.

I therefore gave my first attention to the selection of some more suitable liquid. The ideal one ought to have small "volume heat,"* and should be a perfect insulator, and therefore I at first selected aniline. I determined its specific heat over a range of from 15° to 52° C., and found that in some respects it suited my purposes admirably. A full description of this work will be found in paper A.

Early in September I had, in consequence of an accident, to take the calorimeter to pieces and withdraw the aniline. I was then alarmed by the darkening in colour which it had undergone. In the discussion on the paper above referred to, Dr. Armstrong expressed his opinion that the change in constitution indicated by this change in colour was not of a nature to render it likely that it would produce any appreciable effect on the specific heat, as it was probably due to the formation of a body whose properties were similar to those of aniline. I may add that Professor Ramsay independently expressed an opinion to the same effect. My observations show that no alteration in the specific heat of aniline had been indicated by the change in colour referred to, and I am still of opinion that it may be regarded as a liquid admirably adapted for calorimetric purposes, as it is but rarely that it would be required for experiments extending over a period of months or years.

If I am able to carry out my investigations into the latent heat of evaporation of water and other liquids according to the plan I have designed, it is probable that the enquiry will occupy my leisure time for some years, and as the exact determination of the capacity for heat of the calorimeter and contents throughout a large range of temperature is a most laborious one, I was anxious to employ some liquid about the constancy of whose composition I should have no anxiety.

At this time, Mr. Thomas suggested to me that I should try a particular kind of petroleum oil supposed to consist of hydrocarbons only. This is a singularly limpid oil, without colour, smell, or taste. I tested its insulating powers very severely over a range of temperature 10° to 130° C., and although I placed two large electrodes within a quarter of an inch of each other, and used a potential difference of 10 volts, I could cause no permanent deflection in a high resistance galvanometer throughout this range of temperature. Its specific gravity at 15° is .865, and, as I shall show hereafter, its "volume heat" is smaller than that of aniline.† After several experiments of different kinds, I came to the conclusion that this oil was a most suitable liquid for my purpose.‡

The replacement of aniline by oil necessitated a re-determination of the capacity

* I propose to use the above term to denote the capacity for heat of any volume of a substance as compared with the capacity for heat of an equal volume of water. The phrase has already been used in a similar sense by Deeley, "Chem. Soc. Journ.," 1893, p. 854.
† This oil appears to me to be well adapted to many physical purposes.
‡ See note at end of this Section.
for heat of the calorimeter and its contents throughout my range of temperature, and as far as regards the purposes of the present enquiry, a great portion of my work on aniline was rendered useless. The method employed during the aniline investigation necessitated a repetition of the experiments with different masses of aniline and with different electromotive forces. As, however, those experiments had given me a very exact determination of the capacity for heat of the calorimeter itself throughout the range of temperature 15° to 52° C., the whole of the labour had not to be gone through again, for (the "water equivalent" of the calorimeter being known) it was not necessary, when using oil, to repeat the experiments with different masses.

In Appendix II., I give particulars of the method employed for determining the capacity for heat of the calorimeter and contents at different temperatures.

The following table gives the results, and as the value of the specific heat of this oil at different temperatures may be of use to other experimenters, I have also given (in terms of a thermal unit at 15° C.) the capacity for heat \( C_h \) of calorimeter and contents at temperature \( \theta_l \) (N scale), and the specific heat of the oil \( S_l \). The mass of oil (corrected to \textit{vacuo}) = 474.02 grams.

<table>
<thead>
<tr>
<th>( a_l )</th>
<th>( C_h )</th>
<th>( S_l )</th>
<th>( .4830 + (\theta_l - 29) \times .00087 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>307.50</td>
<td>4830</td>
<td>4830</td>
</tr>
<tr>
<td>30</td>
<td>312.38</td>
<td>4917</td>
<td>4917</td>
</tr>
<tr>
<td>40</td>
<td>317.79</td>
<td>5006</td>
<td>5006</td>
</tr>
<tr>
<td>50</td>
<td>323.14</td>
<td>5092</td>
<td>5091</td>
</tr>
</tbody>
</table>

The tables in Appendix II. show that the numbers in Column III. are \textit{direct experimental results}, not "smoothed" in any way.

It is noticeable that the value of \( S_l \) is a linear function of \( \theta_l \) throughout the above range, although the curvature of the line giving the capacity for heat of the calorimeter is very marked.

Probably these results are correct to better than 1 in 1000 (see Appendix II.), but, as an inspection of Table II. will show, an order of accuracy of 1 in 10 would have been sufficient. As, however, the accurate determination of \( C_h \) and \( S_l \) involved (by the method adopted) little more labour than an approximate determination, I thought it advisable to ascertain the specific heat of the oil with accuracy.

Since \( \Sigma q = C_h \{(\theta_l - \theta'_o) + (d' - d'')\} \) and \( C_h \) varied from 307 to 323, it is obvious that if \( \Sigma q \) was to be kept small, the changes in \( \theta_l \) and \( d \) must be very limited, and that such changes must be measured with extreme care. Having already described the manner in which the temperature of the surrounding walls was kept constant, and the way in which any small variations in \( \theta_l \) were ascertained, I now indicate the method of measuring the values of \( d' \) and \( d'' \) (i.e., the initial and
HEAT OF EVAPORATION OF WATER.

final differences between the temperature of the calorimeter, \( \theta_1 \), and that of the surrounding walls, \( \theta_2 \).

As differences of temperature had now to be dealt with, the use of differential thermometers naturally suggested itself.

The following extract is taken from a full description of these thermometers given in my Paper A. (see also Plate 6, fig. 2):—

"Two platinum thermometers (labelled AB and CD) were constructed with great care; four stout platinum leads passed down the stem of each, supported and insulated in the usual manner by small disks of mica, and the resistance of all these leads was made as equal as possible before attaching the coils. Great attention was given to this matter, and it is probable that the leads in no case differed amongst themselves by 1 in 10,000. The coils, consisting of a particularly pure sample of platinum wire, were then attached, and several days were devoted to securing their equality. Their resistance in ice was about 18 ohms, thus \( \frac{1}{1800} \) of their resistance could be directly determined on the box. The galvanometer swing was about 500 for a change of \( \cdot01 \) in the box; and such equality was secured that when both thermometers were placed in ice (the necessary precautions being taken with regard to exterior connections, &c.) no readable difference in the swing of the galvanometer could be observed; thus they differed by a quantity certainly less than 1 in 100,000. This equality, although not a necessity, was a great convenience.

"Although cut from the same length of wire, and insulated in a precisely similar manner, the coils did not possess exactly the same coefficients. The resistances in steam and sulphur were repeatedly determined and checked by observations in the vapour of aniline. Both thermometers were on several occasions heated to a red heat, the hard glass tubes containing them becoming slightly bent in the process; but, since this annealing, no further change has been observable in them. The method of completely standardising such instruments has been fully described by Professor Callendar and myself in 'Phil. Trans.' 1891, A, and I need not, therefore, here dwell upon it. The values of \( S \) differed slightly, viz., 1.513 and 1.511; but such a difference, even if not allowed for, would, over the range 0° C. to 100° C., in no case cause an error exceeding about \( \frac{1}{2000} \)° C. in elevation. These thermometers were so connected that the compensating leads of AB were placed in series with the coil of CD, and \( \text{vice versa} \). Any heating of the stem of AB or CD, therefore, added an equal resistance to each arm of the bridge; and, as the leads were everywhere bound together, the indications were absolutely independent of all changes in temperature except those of the bulbs.

"The two thermometers, with their leads connected as described, were placed at opposite ends of a bridge-wire of platinum-silver. During the spring of this year this wire was subjected to a most careful calibration by what was practically Carey Foster's method, and it proved to be more unequal than I had expected. It was therefore re-calibrated by a different method in which a resistance-box was used
as a shunt, and the agreement between the results was satisfactory. The whole wire was 80 centims. long and had a total resistance of about 0·4 ohm. For convenience, and to avoid thermal effects, a similar wire connected with the galvanometer was laid alongside it, and the sliding-piece was fitted with a screw so arranged that a small turn of the screw-head made contact with both wires.

"The wire and contact maker were covered by a thick copper shield (the screw-head projecting through a narrow slot) passing from end to end of the bridge. Thus the temperature of the wire was kept uniform. By means of a vernier, the divisions on the scale could be read to $\frac{1}{10}$ millim., which with this wire and thermometers $AB$ and $CD$ indicated at 50° C. a temperature difference of 0·00915° C. The temperature coefficient of this wire was found to be 0·0029. The resistances of the different parts of the wire were, after correction for the errors of individual coils, &c., merely expressed in terms of the mean box ohm, the absolute value being of no consequence so long as the fixed points were determined in terms of the same standard. The remaining two arms of the bridge were constructed of german-silver. They were wound together, boiled in paraffin, placed in a bottle, and I expended much care in finally adjusting them until equal. Their resistance was about 5 ohms, and that of the galvanometer about 8 ohms, which, assuming the resistance of the thermometers as about 20 ohms each, would give nearly the maximum of sensitiveness. A single storage-cell was always used, and a resistance of 40 ohms was placed in the battery circuit when the thermometers were in ice. A table was then calculated which gave the resistance necessary in the battery circuit when the thermometers were at any temperature in order that $C' R$ (where $R$ is the thermometer resistance) should be constant. Thus the rise in the temperature of the thermometer-coils due to current-heating was always the same, and consequent errors were eliminated, a point to which I attach considerable importance.

"The value of $R_1 - R_0$ in thermometer $AB$ was 6·88815; therefore a difference of 1 ohm at 50° C. indicated a difference of 14°·5177 C., and as

$$\frac{dp}{dt} = \left\{ 1 - 8 \frac{2t - 100}{100^2} \right\},$$

the degree value of any bridge-reading at other temperatures can be deduced.

"There was no difficulty, in the arrangement above described, of reading with certainty a difference of $\frac{1}{1000}$° C., and, as an illustration, I may mention the fact that if the thermometers were placed in separate hypsometers side by side on the bench and one of the hypsometers was then removed to the ground (about 3 feet below), the difference in the bridge-wire reading thus caused slightly exceeded 0·4 millim."

In the paper above referred to, further particulars are given regarding the standardisation of these thermometers. During the experiments there described they were used to determine the rate of rise in the temperature of the calorimeter, whereas, in the work I am now describing, they were used chiefly as detectors of any
difference of temperature between the calorimeter and the surrounding walls, and I
therefore omit the details of the determination of their fixed points, &c., although I
must add some other facts which are of importance for the present purpose.

The bridge-wire scale was so fixed that the mark 60 centims.* fell exactly in the
middle. Had the bridge-wire been uniform therefore, and had the coefficients of the
two thermometers been always the same, then when both were at the same tempera-
ture the bridge-wire reading would necessarily have been always 60 centims. I
have stated that the thermometer resistances might be regarded as practically equal
when both were in ice. The bridge-wire reading, however, was found to be 598·35
millims., when AB and CD were both in ice. At first sight this appeared to indicate
a difference in the resistances of the two thermometers at 0°, but when the
 calibration of the bridge was concluded, it gave 598·4 millims. as the middle point of
the bridge and thus afforded independent proof of the truth of the calibration and
of the equality of the coils forming the other two arms of the bridge. Owing to the
slight difference above referred to in the coefficients of the two thermometers the
reading of the bridge null-point was found to be 601·4 millims. when both thermo-
meters were at 100°. Now (as described in Paper A.) the fixed points of these
thermometers in ice, steam, aniline, and sulphur-vapour, had been repeatedly
determined with extreme care. I have, since the conclusion of these experiments
(i.e., on November 4), again taken the values of R₀ and R₁—ice and steam. They
remain practically unchanged and are as follows:—

<table>
<thead>
<tr>
<th>AB.</th>
<th>CD.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>24·58526</td>
</tr>
<tr>
<td>R₀</td>
<td>17·69711</td>
</tr>
<tr>
<td>R₁ - R₀</td>
<td>6·88815</td>
</tr>
</tbody>
</table>

Thus the difference between AB and CD would, when in steam, exceed their
difference in ice by 0'00198 ohm. Now the value of 1 millim. of the bridge-wire at
reading 60 was 1'0020 times the mean bridge-wire millim., and the value of the
mean bridge millim. was 0'0062875 box ohm. Thus 1 millim. of bridge-wire at
60 = 0'006300 box ohm. Hence the movement of the two thermometers from
ice to steam ought, according to the standardisation, to have caused a movement
of 183 millims. = 3·1 millims. On placing both thermometers in steam at 100° the
actual bridge-wire reading was found to have altered from 598·35 to 601·40, a

* The scale was marked from 20 to 100 centims.
+ Expressed after correction for individual coil errors, &c., in terms of my “mean-box” ohm
(Paper J., p. 409). The absolute values being of no consequence, I have, in order to save arithmetic,
expressed the resistances of all my platinum thermometers in “mean-box” ohms.
change of 3·05 millims.; thus, entirely independent methods agree in giving the following formula as a sufficiently close approximation for the bridge-wire null-point at any temperature $\theta$, viz.,

$$N.P. = 598·35 + 03\theta.$$ 

True, the coefficient of $\theta$ should be slightly larger, but I did not profess to read the vernier to nearer than '05 millim. during the calibration of the wire, and therefore any closer approximation would be useless.

As even a small difference between the average temperature of the calorimeter and the surrounding walls would have some effect in experiments lasting more than an hour, the agreement between the results obtained by the different methods above described was extremely satisfactory. In addition I carried out a series of observations with both thermometers strapped together and immersed in the rapidly-stirred tank water, the temperature of which was gradually raised from 15° to 54°, and the position of the bridge-wire null-point was found throughout that range to be accurately given by the above formula.

The galvanometer was observed by means of a microscope fitted with a micrometer eye-piece by Zeiss. The swing was very "dead beat" and very uniform for a given D.P. The $\frac{1}{10}$th of a division could be estimated without difficulty by anyone accustomed to the instrument, and it was found more convenient to read and enter swings with $\frac{1}{10}$th of a division as unity rather than to express the fractions as decimals. Thus a swing of 2·5 divisions was entered as 25. I mention this as otherwise the swings given in the tables might appear curiously large. Occasionally the swing due to a change of 1 millim. in the bridge-wire reading was observed, but as the E.M.F. used was constant, and the galvanometer control-magnet was not re-adjusted during these experiments, the swing for a given change was found to remain practically constant when the temperature of the thermometers was unchanged. As the resistance of two arms of the bridge altered when $\theta$ altered, the swing varied slightly when $\theta$ changed, but the arrangement, above described, for keeping $C^2R$ constant, diminished the extent of this change. A swing of 90 corresponded to a change of 2 millims. in the bridge-wire reading when $\theta = 40^\circ$, and the swing at 30° was about 94.

The swing was of course obtained by reversing the battery connections and was thus independent of thermal effects, changes in the position of the galvanometer zero-point, &c.

Now, as above stated, a change of 1 millim. of bridge-wire about the reading 60 centims. indicated a difference of '0006300 box ohm. If therefore the bridge-wire reading was at the null-point a swing of 10 indicated a difference of $\frac{10}{3}$ of '0006300 = '000140 ohm in the resistance of the two thermometers.

The following Table (calculated from the constants of the thermometers by means
of the formula on p. 286) gives the change in temperature (on the N scale) corresponding to a change of 0.1 box ohm in thermometer AB.

**Table IV.**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>(\Delta R) (box ohms).</th>
<th>(\Delta pt.)</th>
<th>(\Delta \theta.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>1.4518</td>
<td>1.4387</td>
</tr>
<tr>
<td>20</td>
<td>0.1</td>
<td>1.4518</td>
<td>1.4430</td>
</tr>
<tr>
<td>30</td>
<td>0.1</td>
<td>1.4518</td>
<td>1.4474</td>
</tr>
<tr>
<td>40</td>
<td>0.1</td>
<td>1.4518</td>
<td>1.4518</td>
</tr>
<tr>
<td>50</td>
<td>0.1</td>
<td>1.4518</td>
<td>1.4518</td>
</tr>
</tbody>
</table>

Now the value of the mean millimetre of the bridge-wire (at temperature 15°) was 0.00062875 box ohm, hence the following Table which (col. 2) gives the difference in \(\theta\) indicated by a difference of 1 mean bridge-wire millim. from the bridge-wire null-point at the given temperature, and (col. 3) the difference in temperature indicated by a swing of 10 when the contact-maker is on the null-point.

**Table V.**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>(\Delta \theta) for difference of 1 mean millim. b.w.</th>
<th>(\Delta \theta) for swing of 10.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.009046</td>
<td>0.001865</td>
</tr>
<tr>
<td>20</td>
<td>0.000073</td>
<td>0.001930</td>
</tr>
<tr>
<td>30</td>
<td>0.000101</td>
<td>0.002022</td>
</tr>
<tr>
<td>40</td>
<td>0.000128</td>
<td>0.002074</td>
</tr>
</tbody>
</table>

Before an experiment, the contact-maker was set, with the aid of a magnifying glass, to the exact null-point corresponding to the temperature at which the experiment was to be conducted, and it was left untouched throughout the experiment.†

The initial and the final swing rarely exceeded 30 or 40, and could certainly be read with a limit of error of 2, when only one observation was taken, and as, at these times, three observations were meant (they were, by the way, usually identical), the

* As AB was the thermometer immersed in the calorimeter it is with changes in its temperature that we have chiefly to do.

† An error of 0.05 millim. in the setting of the bridge-wire contact-maker would correspond to a difference of 0.00455° at 40°, and the radiation, &c., due to such a difference would be negligible. The radiation, &c., coefficient of this calorimeter when full was about 0.00009 per 1° per sec., or the loss in temperature due to a difference of 1° would be about 324° = 100.4 thermal grams per hour (assuming the capacity as 310), thus a difference of 0.01° throughout an experiment would have caused a loss or gain of 1 thermal gram. Of course, the differences in temperature rarely attained to 0.01°, and again, the differences were alternately + and –, so that the radiation, &c., loss or gain was evidently negligible. The radiation, &c., coefficient can be deduced from the experiments on the rate of rise made when determining the value of \(C_h\) (Appendix II.).

MDCCXXCV.— A.
probable error was certainly less than 2, and, I believe, less than 1. Assume the probable error to be as great as 2, it follows that the differences of temperature could be determined to °0004°, and I am confident that differences of °0001° could be detected.

There can be little doubt therefore that the quantity \( \Sigma q = C \left\{ (\theta_0 - \theta_0') + (\theta'' - \theta'') \right\} \) could be determined to a far higher degree of accuracy than subsequent experience proved to be necessary.

Note.—December 4, 1894. At Mr. Heycock's suggestion, I have to-day tested as follows the oil supplied to me by Mr. Thomas, and referred to in the preceding section. We placed a lump of sodium in a test-tube filled with the oil, and gradually raised the temperature to above 160° C. No action whatever was visible, and the surface of the melted sodium remained as bright as that of pure mercury. We may assume, therefore, that the manufacturers are justified in their statement that it consists of hydrocarbons only, and the probability that different samples would possess approximately the same composition is sufficient to make the determination of its specific heat of some value.

Section VII.—The Heat due to the Stirring (\( Q_s \)).

I have already pointed out the necessity for rapid stirring. Throughout these experiments the stirrer revolved at a rate of about 310 to 320 revolutions per minute, which is a slow rate as compared with that adopted during my enquiry into the value of \( J \). The conditions, however, are different. In my former work I had at times to make observations with the calorimeter only partially filled with liquid, and I found that unless the water was thrown over every part of the calorimeter, its capacity for heat varied with the depth of the liquid. Throughout my present work the calorimeter was full, the liquid almost touching the lid, and, in consequence, I considered the slower rate sufficient to ensure an even distribution of temperature.

In my aniline experiments previously referred to, I eliminated the effect of the stirring-heat by finding the temperature \( (\theta_s) \) at which the stirring supply exactly balanced the loss by radiation, &c., and thus the rate of rise at \( \theta_s \) enabled me to determine the effect of the electrical supply. As throughout my observations on latent heat I had to maintain the temperature of the calorimeter at an equality with the surrounding walls, this mode of elimination was not applicable.

Two methods of finding the value of the mechanical supply suggested themselves.

I. That of finding the mass of water which it was necessary to evaporate per hour in order to maintain the calorimeter at a constant temperature, when the supply of heat was that due to the stirring only.

II. That of determining the rate of rise across the null-point \( (\theta) \) when the heat supply was that due to stirring only; \( (b) \) when the heat was due to the stirring and a given potential difference.
HEAT OF EVAPORATION OF WATER.

I. I made a large number of determinations by this method, especially during the "preliminary experiments," of which an account is given in Section IX., where the evaporation was promoted by passing a current of dry gas through water.

As I shall give details of the operations when describing the "preliminary experiments," I will not enter into particulars here, but I may now mention that the results by this method were by no means satisfactory, either as regards the determination of the stirring heat supply \(Q_s\) or of the values of \(L\). The discrepancies in the value of \(Q\) are, however, not alone sufficient to explain the comparative failure of this method of finding \(L\), for when both the rate and the temperature were the same, the variations in \(Q\) never attained to 1 in 20, and as \(Q\) was but about one-hundredth of the total supply, the approximation was nearly sufficient. I omit any detailed account of these experiments, as I made no use of them in my final calculations, and it would needlessly fill much space. I will, however, give the conclusions they led to, as they corroborate the results obtained by the method finally adopted.

Let
\[
m_s = \text{mass of water evaporated per 1 second by the stirring supply},
\]
and
\[
r = \text{the rate of stirring (i.e., number of revolutions per second}).
\]

When \(\theta_1\) diminished, the value of \(m_s\) increased, and this rate of increase was much greater after the aniline was replaced by oil; the change being evidently due to the increase of viscosity as the temperature diminished. When the stirring took place in aniline \(m_s\) varied very nearly as \(r^3\), but when oil was the liquid \(m_s\) varied nearly as \(r^4\).

In a former paper\(^*\) I have proved that when the liquid was water the stirring heat varied almost exactly as \(r^3\), and I gave particulars of 108 experiments bearing out that conclusion. Again, in Paper A., I have shown that when using aniline with a different form of stirrer \(Q_s \propto r^3\) approximately. Now with the same stirrer as that used in aniline we get with oil \(Q \propto r^4\); at 50° the power of \(r\) should be slightly higher, at lower temperatures rather smaller. These differences, although surprising, are none the less real.

In the case of water the conditions were so different (e.g., \(r\) was about 30 instead of about 5) that no comparisons could be drawn, but, in the case of the aniline and the oil, the conditions were almost identical. My incredulity with respect to the relations between \(Q_s\) and \(r\) led to considerable delay, as I repeated these experiments unnecessarily, and it was not until a different method of observation led to the same conclusion that I felt any confidence in the results.

II. I now pass to the method indicated in II. (supra), in which no weighings were involved, and where I was also able to dispense with the passage of air through the apparatus.

\(^*\) Paper J.

2 p 2
Let \( t \) be the time of rising through a small range of temperature from below to above the surrounding temperature \( (\theta_0) \).

If the heat supply is in one case due to both an electric current and the stirring, and in another to the stirring only, we have

\[
(d\theta_1/dt)_e = (d\theta_1/dt)_s = (d\theta_1/dt)_c.
\] (I.)

where \( \theta_1 \) is the temperature of the calorimeter, and the suffix denotes the nature of the supply.

And (using the notation on pp. 272 and 273)

\[
(d\theta_1/dt)_e = Q_e/C_{e_1}, \quad \text{and} \quad (d\theta_1/dt)_s = Q_s/C_{s_1},
\]

therefore

\[
\frac{Q_e}{Q_s} = \frac{(d\theta_1/dt)_e}{(d\theta_1/dt)_s - (d\theta_1/dt)_c} = f
\] (II.).

Eq. (II.) will be true on any scale, and thus it is unnecessary to convert the bridge-wire readings into degrees C., and since

\[
Q_s = fQ_e
\] (III.),

if \( e, n, \) and \( R_1 \) be known, we can find \( Q_s \), for

\[
Q_s = e^2n^2/R_1J
\] (IV.).

Thus \( Q_s \) can be found, although the capacity for heat of the calorimeter and contents and also the scale of temperature are unknown.

If we convert the bridge-wire degrees into C. degrees (N. thermometer) then, since

\[
(d\theta_1/dt)_e - (d\theta_1/dt)_s = Q_e/C_{e_1},
\]

we get

\[
C_{s_1} = \frac{Q_e}{(d\theta_1/dt)_e - (d\theta_1/dt)_c}
\] (V.),

and thus \( C_{s_1} \) can be found.

In Appendix I. I give particulars of the experiments by which the values of \( Q_s \) for different values of \( \theta_1 \) were found. I regret that the observations are so few in number. Unfortunately I did not adopt this mode of experiment until the eleventh hour, and as these experiments were very lengthy, I should consequently have been unable to complete sufficient direct determinations of \( L \) to establish its value at the two points to which want of time compelled me to limit the investigation.

On comparing the results with those obtained in oil by the previous method, I found that the agreement was sufficiently close to warrant a postponement of further
investigation on this point, and I am confident that the values of \( Q \), given in the following table are correct to better than 1 in 50, at temperatures 30° and 40°, although I am less certain about the values at 20° and 50° C. The latter, however, are not required for the purposes of this paper, except in so far as they affect the specific heats of the oil in Table III.

**Table VI.**—Thermal grams per sec. \((Q_s)\) at rate \((r)\) 5·300 revolutions per sec.

<table>
<thead>
<tr>
<th>( \theta_t )</th>
<th>( Q_s )</th>
<th>( \frac{Q_s}{r_t} = k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0·02235</td>
<td>298 ( \times 10^{-8} )</td>
</tr>
<tr>
<td>40</td>
<td>0·00466</td>
<td>590 ( \times 10^{-8} )</td>
</tr>
<tr>
<td>30</td>
<td>0·00665</td>
<td>843 ( \times 10^{-8} )</td>
</tr>
<tr>
<td>20</td>
<td>0·00834</td>
<td>1056 ( \times 10^{-8} )</td>
</tr>
</tbody>
</table>

Let \( Q'_s \) be the thermal grams per second due to a rate \( r_t \).

Then

\[
\frac{Q'_s}{r_t^4} = \frac{Q_s}{r_t^4} = k, 
\]

therefore

\[
Q'_s - Q_s = k (r_t^4 - r^4),
\]

therefore

\[
Q'_s = Q_s + k (r_t^4 - r^4) \quad \ldots \ldots \ldots \ldots (1).
\]

Hence

Temperature 40°, then \( Q'_s = 0·00466 + (r_t^4 - 789) \times 0·000059 \).

,, 30°, ,, \( Q'_s = 0·00665 + (r_t^4 - 789) \times 0·000084 \).

I do not, of course, suppose that \( Q_s = kr^4 \) is the exact relation. I have already indicated that \( r^4 \) was too small at high, and too great at low temperatures. It must be remembered, however, that the variations in \( r \) were small, and thus the relation is sufficiently close for the correction of such variations as occurred during these experiments.

If we assume that the work done (for a given value of \( r \)) is proportional to the viscosity, the values of \( Q_s \) denote how great a change in viscosity is produced by raising the temperature from 20° to 50°. I repeat, however, that the values at 20° and 50° must be regarded with suspicion.

* I have no corroborative experiment (by the former method) at 20°, and only one at 50° (see Appendix II.).
Section VIII.—Measurement of the Heat Developed by the Current (Q.).

A sketch of the electrical connections is given in Plate 6, fig. 3, and a full description will be found in Paper J., pp. 382-388, therefore I will here give only a brief description.

Measurement of E.

Leads marked 2 and 4 were connected with the storage cell circuit, leads 1 and 3 with the Clark cells. A special form of rheochord was used consisting of two long barometer tubes (7 feet in length), which were so arranged that they could be raised or lowered by the rotation of handles; thus the length of the vacuous space could be altered at will. Platinum wires passed down these tubes into the mercury. The wires were placed in parallel arc and thus one acted as a shunt to the other. The change in resistance depended, therefore, not only on the movement but on the ratio of the two resistances, and the instrument could be set so that a large movement caused but little change, or vice versa. The contact between platinum and mercury in vacuo was found to be very satisfactory. The resistance of the storage circuit could thus be altered at will. The Clark cell circuit contained a high resistance galvanometer G₁, with a resistance of about 9000 ohms, and joined the storage circuit at the roof of the calorimeter (at M and N, small sketch, Plate 6, fig. 3). By adjusting the rheochord the ratio of the external resistance of the storage circuit to the coil resistance could be altered at will, so that the D.P. at the ends of the coil became equal to that of the Clark cells, and the balance was maintained by watching the indications of G₁, and, when necessary, adjusting the rheochord. The spot of light from G₁ passed down a tunnel 4 feet in length on to a sheet of ground-glass placed opposite the rheochord. In Paper J., p. 384, I have given the experimental numbers on which the following statement was based:—

"It thus appears that the variations in E (the potential difference at the ends of the coil) were certainly within $\frac{1}{100,000}$ of the mean value during the experiments, and changes in E, consequent on changes in the coil resistance, or the E.M.F. of the storages, could be disregarded."

The effect of any error in determining E would be serious (the quantity $E^2$ being used in the reductions), and hence its accurate measurement was of great importance. I am satisfied, however, that (assuming the value of E for the Cavendish standard Clark cell to have been accurately determined) no error in the measurement of Q is due to uncertainty as to the potential difference. The thirty-six Clark cells used have been fully described, in Paper J., pp. 385-388, as well as in the Paper by Messrs. Glazebrook and Skinner.* They have been compared with each other at regular intervals up to the present time, and their relative changes are small. At least three of these cells were always placed in parallel arc. Sometimes when

* "Phil. Trans.," A, 1892, pp. 622-624.
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working with a D.P. of four cells at least sixteen were really in use. Throughout these experiments they were maintained at a temperature close to 15° C., by a regulator which warmed the tank when below 15° C. and turned tap-water through the tank when above 15° C. As full particulars are given in the pages of Paper J., I think the above summary will be sufficient.

There is one alteration in the electrical connections to which I wish to draw attention. In former experiments some time always elapsed, after the current was established, before any observations were taken. It, however, appeared probable that in this work I should occasionally have to cut off and put on the current during an experiment. For some time after the establishing of the current, a constant re-adjustment of the rheochord was required, as the temperature of the wires, &c., forming the external circuit was gradually raised, and the external resistance in consequence increased. During this period of adjustment the balance could not be as accurately maintained as when the temperature of the external wires had become steady. In order to avoid this preliminary adjustment, a coil of the same wire and resistance as that in the calorimeter was constructed and placed in a tube containing the same oil as that in the calorimeter, and this tube was fixed in the tank at F (Plate 6, fig. 3).

At $k_1$ a key was so arranged that one movement brought the storages into connection with the calorimeter coil by means of leads 2 and 4, while another movement caused the current to leave the calorimeter circuit and pass through F. A second key (not shown in fig. 3) enabled the Clark cell to be also connected to F. The current was sent through F for 10 minutes or so and the balance adjusted, before an experiment commenced. On moving the key at $k_1$, the current was switched on to the calorimeter, the Clark cell circuit was then also shifted and the balance once more made perfect. Thus the current through the externals was kept constant whether it was passing through the calorimeter or not, and therefore the rheochord required far less manipulation.

Again, the key $k_1$ was so arranged that whenever the current was shifted, a connection in a chronograph circuit was established, and thus the times of "making and breaking" the calorimetric current were automatically registered. True, the marked time was in each case a fraction of a second before the "make and break," but the actual duration of the intervals was truly recorded.

Measurement of $R_1$.

The holes in the paraffin blocks $P_1$ and $P_2$ (Plate 6, fig. 3) contained mercury. Connection could be made by two cross pieces of copper rod, between either of the slots in $P_1$ and any of the holes in $P_2$. These copper rods, when in position, rested on the wires which passed through the bottom of the holes. Denoting the resistance of the coil by $R_1$, that of the leads from $P_2$ to the lid of the calorimeter by $r_1$, $r_2$, $r_3$, $r_4$,
it is evident that by a movement of the connecting rods, the following resistances could be taken, viz.:

\[ r_1 + r_2, \quad r_1 + R_1 + r_3, \quad r_2 + R_1 + r_3, \quad r_3 + r_4. \]

If \( N_1, N_2, N_3, \) and \( N_4 \) are the resulting numbers, we get

\[ R_1 = \frac{(N_2 + N_3) - (N_1 + N_4)}{2}, \]

and there is no necessity that \( r_1, r_2, r_3, \) and \( r_4 \) should be equal. The value of \( R_1 \) was always obtained in the above manner, and then expressed in terms of the box ohm at 17°. A full account is given in Paper J., pp. 407–410, of the comparisons of the individual coils of my resistance box with the B.A. Standards, and the values of \( R_1 \) were reduced to true ohms in the manner there indicated, with the further corrections given in a later communication.\(^8\)

In Appendix III. I give an example of an observation together with the reductions.

It was next necessary to find the increase in \( R_1 (\delta R) \) due to the rise of temperature caused by the current. This was done in substantially the same manner as that described in Paper J., pp. 404–407; \( \delta R \) was in this case found to be very small—as shown by the following table.

**Table VII.**

<table>
<thead>
<tr>
<th>Potential difference in terms of a Clark cell.</th>
<th>( \delta R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00076</td>
</tr>
<tr>
<td>2</td>
<td>0.00198</td>
</tr>
<tr>
<td>3</td>
<td>0.00377</td>
</tr>
<tr>
<td>4</td>
<td>0.00650</td>
</tr>
</tbody>
</table>

The resulting curve was (as in other similar cases) practically a parabola.

A further correction was necessary for the heat developed in leads 2 and 4 in the portion that passed from the steel to the calorimeter lid. Their total resistance was 0.0068. We may assume that half the heat here generated passed into the calorimeter, and therefore consider their resistance as 0.0034 ohm = \( r \). Now the points kept at a constant D.P. were between these wires and the coil, and since \( JH = E^2/R \left(1 + r/R \right) t \), we get the effective resistance = \( R - r \).

The following table gives the values (after the application of all corrections) of \( R_1 \) at the temperatures at which the L experiments were performed, the potential difference being denoted by the suffix.

HEAT OF EVAPORATION OF WATER.

Table VIII.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>(R_y)</th>
<th>(R_{xy})</th>
<th>(R_{y})</th>
<th>(R_y')</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>10.3248</td>
<td>10.3266</td>
<td>10.3284</td>
<td>10.3309</td>
</tr>
<tr>
<td>30</td>
<td>10.3482</td>
<td>10.3502</td>
<td>10.3520</td>
<td>10.3545</td>
</tr>
<tr>
<td>40</td>
<td>10.3720</td>
<td>10.3740</td>
<td>10.3758</td>
<td>10.3783</td>
</tr>
<tr>
<td>50</td>
<td>10.3966</td>
<td>10.3986</td>
<td>10.4003</td>
<td>10.4023</td>
</tr>
</tbody>
</table>

\(\delta R_1\) per \(1^\circ\) C. = 0.024.

This coil has shown no signs of any change throughout its history.

As \(Q_e = (ne)^2/R_1 J\), I have now indicated how the value of \(Q_e\) could be accurately ascertained.

Had full details of the method not been given in previously published papers, it would have been necessary for me to give further particulars as to the various measurements.

There can, I think, be little doubt that the value of \(Q_e\) could be determined with great certainty.

I have already (see p. 272 *supra*) pointed out that even if my value of \(J (4.199 \times 10^2)\) be in error, it is the correct value to use for these experiments, and that even if \(e\) (the D.P. of a Clark cell) and the units in which \(R_1\) is measured (*i.e.*, the value of a "true ohm") are in error, the results are unaffected, provided that no changes have taken place in my Clark cells, or the coils of the resistance box since they were used for the determination of the value of \(J\).

[Note, May 4, 1895.—During the spring of this year my Clark cells were carefully re-compared with the Cavendish standard, R I. Comparisons were made at regular intervals, and Mr. Skinner was so kind as to take some independent observations. The differences are expressed in hundred-thousandths of the E.M.F. of the standard. The highest of the thirty cells exceeds R I by 40 such units. The lowest is less than R I by 36. The mean value of the whole set is less than R I by 3 such units (*i.e.*, by 0.00004 volt). Thus, although the individual cells show larger discrepancies than in 1892–4, the mean value is almost exactly that of the Cavendish standard. The previous history of that standard shows that it had remained unchanged during the interval of eight years which had elapsed between the absolute determination of its E.M.F. by Lord Rayleigh in 1883, and that by Messrs. Glazebrook and Skinner in 1891. There is no reason to suppose that it has altered since the latter date, and this conclusion is borne out by comparison with other standards at the Cavendish Laboratory. I think, therefore, that I am justified in assuming that the mean E.M.F. of my cells remains practically unaltered.

Cells 37 to 42 have been compared at Manchester by Professor Schuster with his standard. These six have the highest mean E.M.F. of any of my sets. Their mean value exceeds R I by 22 units, and they exceed Professor Schuster's standard by MDCCXCV. — A.

2 Q
70 units. It would thus appear that 71 exceeds Professor Schuster's standard by 48 units, i.e., by about 0.0007 volt. It must, however, be remembered that between these comparisons the cells had been subjected to several transits by railway.]

Measurement of Time.

The chronograph was controlled by the electric clock described in Paper J. (p. 414). The clock has remained untouched from July 16th to the present day—November 18th, and during that time it has gained 12 minutes, i.e., a gaining rate of about 1 in 15,000. The gain has been regular throughout the interval, the clock being singularly indifferent to small changes of temperature. I therefore consider that the measurements of time require no correction.

Section IX.—The Results of Experiments in which Evaporation was Promoted by the Passage of a Gas.

I have hitherto referred to the experiments I describe in this section as "preliminary" for want of a better name; but I had originally hoped that the method would have given satisfactory results. Although these experiments have had but little influence on my conclusions, I will briefly describe them, as I am yet at a loss to account for their comparative irregularity.

Dry air, or other gas, was forced in a continuous stream through the water to be evaporated; the cooling thus caused was balanced as before described, and the weight of water evaporated determined by the increase in weight of drying bulbs. I wished to adopt this method, because by adjusting the flow of air the rate of loss of heat could be (by proper arrangements) regulated with nicety, and the thermal balance maintained with great accuracy. When water is made to boil by diminished pressure, the regulation of the cooling presents many manipulative difficulties that I was anxious to avoid.

The experiments were conducted as follows. About 20 cub. centims. of water were placed in the flask F (Plate 6, fig. 1),* the water force-pump set going, and the air first passed through the \( \text{H}_2\text{SO}_4 \) bottles and "tower" S, then through the U-tube and drying tower \( \text{P} \)—both containing \( \text{P}_2\text{O}_5 \). It then passed through the 3-way tap \( \text{T}_2 \) into the 30-feet copper coil \( \text{C}_1 \) in the tank water, thus attaining the temperature \( \theta_0 \) of the tank, and after traversing the immersed tap \( \text{T}_3 \) bubbled through the water in the silver flask. The air and vapour now rose up through the 18 feet of silver coil \( \text{C}_2 \) within the calorimeter, passed out through the 4-way tap \( \text{T}_4 \), which was opened in such a manner as to direct the air current into some \( \text{H}_2\text{SO}_4 \) bulbs (not

* This figure is diagrammatic only, and conveys no idea of dimensions or actual position. For example, the coil \( \text{C}_1 \) surrounded the steel vessel, and the 4-way tap \( \text{T}_4 \) was on the same side of the apparatus as the tap \( \text{T}_2 \). The pipes, &c., crossed and re-crossed each other in such a manner as to render any direct representation impossible. The drying bulbs and connections are not indicated in the figure, as they were afterwards replaced by the condenser (B) and manometer (M).
shown in figure) containing the same depth of $\text{H}_2\text{SO}_4$ as the bulbs to be weighed. Thus when $T_1$ was afterwards so turned as to change the direction of the current to the weighing bulbs, no alteration took place in the rate of flow, which was adjusted as required in the following manner. A T-piece (not shown in sketch) was inserted in the tube between the drying tower $P$ and the tap $T_2$. The vertical leg of the T-piece was a wide graduated tube, open at its lower extremity, and immersed in a deep, narrow vessel (a hydrometer jar) filled with $\text{H}_2\text{SO}_4$. If the air pressure within the pipes was greater than that due to the column of $\text{H}_2\text{SO}_4$ above the open end of this leg, the excess of gas bubbled up through the $\text{H}_2\text{SO}_4$ and escaped into the open air. Thus by raising or lowering the vessel the pressure and quantity of air passing through the whole apparatus could be regulated with exactness. I found it possible to so adjust the flow that when the heat supply was $Q_e$ and $Q_n$, the galvanometer showed no change for nearly an hour. A further advantage of this arrangement was that I could close any tap without increasing the pressure within the apparatus, the whole of the gas then passing out through the regulator. The pressure of the gas near the flask was read on the manometer $M_1$, which had two wide bulbs near the base, the mercury filling the lower bend and three-quarters of the bulbs. The narrow tube on the scale side contained water resting on the mercury, and thus a very open scale was obtained. The instrument was carefully standardised, and a movement of 7.78 centims. in the water level corresponded to a change in the pressure of 1 centim. of mercury. The water was completely cut off by the mercury from all communication with the gas tubes.

The electric connections having been made and the rheochord adjusted until the high resistance galvanometer ($G_1$) showed that the D.P. at the ends of the coil was that of the Clark cells (I shall speak of this hereafter as the "electrical balance," and of the adjustment of the loss or gain of heat as the "thermal balance"), the gas flow was then diminished until the platinum thermometer galvanometer showed that $\theta_4$ slightly exceeded $\theta_0$ ($\theta_1 =$ calorimeter temperature, $\theta_0 =$ temperature of surrounding walls). The current was then switched on to the alternative coil $F$ (fig. 3), $\theta_1$ now decreased and at the moment when $\theta_1 = \theta_0$ the current was switched back again, the key itself recording the time on the chronograph tape. About the same time, the 4-way tap $T_4$ was turned so as to cause the escaping gas to pass through the weighing bulbs. This time had not to be recorded, nor was there any necessity that it should be nearly or at all coincident with the time of establishing the electric current. If, however, $\theta_1$ did not exactly equal $\theta_0$ at the moment of turning $T_4$, the swing of the galvanometer was recorded and the tap only closed at the end of an experiment when the swing was identical with the initial one.

When necessary the thermal balance was maintained for 1, 2, or, in some cases, 3 hours by adjusting the flow of gas. At the close of an experiment $\theta_1$ was again allowed to rise slightly above $\theta_0$, the current switched off (again itself recording the time) and as $\theta_1$ descended the tap was turned back to its old position when $\theta_1 = \theta_0$. 

$2 \varphi 2$
or when the swing was the same as the initial one. The taps $T_2$ and $T_4$, were then turned so that the dry air instead of passing through the tank, &c., went straight through $T_4$ to the weighing bulbs, and thus any moisture left in the connecting tubes was swept into the bulbs.

The swing of the galvanometer was rarely as much as 50 (indicating a difference of about 0°01 between $\theta_1$ and $\theta_0$) throughout one of these experiments, and when such oscillations occurred care was taken to alter the adjustments so that a swing to the right was invariably followed by a similar swing to the left. The whole apparatus could easily be managed by two observers and, on occasions, it was unnecessary to make an alteration of any kind for half-an-hour at a time.

As before stated, the stirrer automatically recorded on the chronograph tape the time of each 1000 revolutions.

The weighing bulbs were of peculiar construction and specially designed for this work. The gas passed through four washings of $H_2SO_4$ and then through a tube of $P_2O_5$, on the further side of which was attached a $CaCl_2$ tube. The latter was not included in the weighings, but only used to prevent any access of the laboratory air to the $P_2O_5$ when the gas current was not passing. The weighing bulbs were connected with the exit tube by a mercury trap* and had simply to be lowered into place, no fitting of rubber tubes being necessary. To avoid condensation, the mercury trough and also the whole of the exit tube exterior to the tank were maintained at a temperature above $\theta_0$ by means of small gas jets.

At the close of an experiment the weighing-bulbs were removed (with their precisely similar tares) to the balance case. A careful weighing was made about an hour after the experiment, and again next morning; an apparent increase of about 0005 gram generally presenting itself.

As (especially in the stirring experiments) small differences in weight had to be measured, I took every precaution I could devise, and I also followed the suggestions of friends whose experience in this matter was greater than my own. The balance was a short-beam one by Verbeck and Peckholdt, and was constructed so as to give a swing of 2:5 divisions per 1 milligram when loaded up to 500 grams. The actual weights to be measured were about 120 grams. I made special efforts to keep the temperature of the balance case steady, and noted the effects of changes in temperature on the ratio of the arms, etc.

The weights used were by Messrs. Oertling, and re-standardised by them last year. The increase in weight during the electrical experiments varied from 08 to 05 grams, the increase during the stirring experiments from 06 to 08 gram.

I think it certain that the weighing error was never so much as 002 gram, and it was probably much less; thus I do not believe that any discrepancies in the values of $L$ greater than 1 in 1000 can be due to errors of this description.

As before described (p. 291) the mass of water evaporated by the stirring supply was

* Neither bulbs nor trough are shown in fig. 1, Plate 6.
determined in a similar manner. Thus, if \( m_s \) be the mass evaporated per second by the stirrer, we have (using the same notation as before)

\[
ML - m_s t = Qe_t + \Sigma q.*
\]

I spent some weeks over these experiments, but the results were so uncertain, that at last I was compelled to give up all hopes of attaining my object by this method. I will therefore omit details and give results only.

**Table IX.**—Evaporation Caused by Passing Dry Gas.

<table>
<thead>
<tr>
<th>Date</th>
<th>Number of Clark cells</th>
<th>Temperature</th>
<th>L.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>September 2</td>
<td>2</td>
<td>49.54</td>
<td>567.5</td>
<td>Calorimeter filled with aniline</td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>49.54</td>
<td>564.4</td>
<td>&quot; &quot; &quot; &quot; oil</td>
</tr>
<tr>
<td>&quot;</td>
<td>11</td>
<td>50.01</td>
<td>566.6</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>11</td>
<td>50.00</td>
<td>566.6</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>11</td>
<td>50.00</td>
<td>567.8</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>49.82</td>
<td>566.5</td>
<td></td>
</tr>
<tr>
<td>August 29</td>
<td>2</td>
<td>39.98</td>
<td>576.9</td>
<td>Calorimeter filled with aniline</td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>39.97</td>
<td>572.2</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>3</td>
<td>39.98</td>
<td>574.5</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>3</td>
<td>39.98</td>
<td>572.9</td>
<td></td>
</tr>
<tr>
<td>September 2</td>
<td>2</td>
<td>39.99</td>
<td>569.8</td>
<td>Oil in calorimeter</td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>39.99</td>
<td>572.9</td>
<td>&quot; &quot; Nitrogen passing</td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>39.98</td>
<td>569.9</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>40.01</td>
<td>572.2</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>40.00</td>
<td>569.4</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>2</td>
<td>39.98</td>
<td>572.7*</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>39.99</td>
<td>572.4</td>
<td></td>
</tr>
<tr>
<td>August 19</td>
<td>1</td>
<td>24.97</td>
<td>582.6</td>
<td>*Nitrogen passing</td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.96</td>
<td>580.6</td>
<td>Calorimeter filled with aniline</td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.96</td>
<td>584.2</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.96</td>
<td>581.7*</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.97</td>
<td>580.0</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.97</td>
<td>584.7</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.95</td>
<td>581.5</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.95</td>
<td>580.3</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1</td>
<td>24.95</td>
<td>581.4</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>24.96</td>
<td>581.9</td>
<td></td>
</tr>
</tbody>
</table>

* \( \Sigma q \) in this case = \( C_s \left\{ (\theta' - \theta'' \omega) + (\bar{d} - d') \right\} + C' \left( T' - T'' \right) \) where \( C_s \) is the "mean mass" of the water in the flask, and \( T' \) and \( T'' \) the initial and final temperatures of that water as indicated by the flask thermometer \( \theta \).
I have included in the above table all the experiments with the exception of two, which were performed on the same day (September 3rd), and whose extreme divergence from the others led to the discovery that the insulation of one of the leads had fallen off. In consequence, the value of $R_1$ was uncertain. Between September 3rd and 11th the whole apparatus was taken to pieces and fitted with new leads and insulators. From this time onwards the calorimeter was filled with oil in place of aniline (see Paper A., p. 77).

I think it is evident that the discrepancies are greater than can be accounted for by errors in weighing, as they sometimes amount to nearly 1 per cent.

At first suspected that some moisture was escaping uncaught by the weighing bulbs, or that the entering air was not dry. I believe, for two reasons, that this was not the case. (1) The $P_2O_5$ bulb, through which the gas finally passed, in no case increased in weight by as much as $0'0040$ gram, and usually only by about $0'0020$ gram, which showed how completely the moisture had been removed by the $H_2SO_4$. (2) Before entering the apparatus the gas passed also through $H_2SO_4$ and $P_2O_5$, therefore any quantity of moisture which escaped these drying agents would be likely to also escape the similar agents at the exit-end, and thus would not affect their weight. I had good evidence that this was the case, for I thoroughly dried the flask and tubes at a temperature of 40°, and then passed the gas through the apparatus into the weighing bulbs for an hour and a half; but the increase of weight in that time was not as much as $0'0005$ gram. Again, if the gas was more completely dried at one end than at the other, the effect would have been to make all the values of $L$ too low or too high. Of course, I was entirely in the dark at the time of these experiments as to the real value of $L$, but I now find that the mean of each group gives a close approximation to the true value, hence there was no permanent raising or lowering cause at work.

It will be noticed that the rate of flow of air was greatly changed during these experiments; when three cells were used the rate of evaporation had to be nine times as great as when the D.P. was that of one cell. Inspection of the table will show that the variations in the values of $L$ do not appear to be functions of the rate.

For some time I fancied that "priming" might be taking place, but, if so, the experiments with a rapid flow would probably all have given lower values than those with a slow flow, the carrying of particles of unevaporated water being much more probable when the velocity of the gas current was increased nine times.

Again, it has been suggested that, as the pressure of the gas diminished during its passage through the apparatus, some heat would in consequence disappear. I would point out that the only constricted portions of the passage (after the air had once entered the tank) were within the calorimeter, and, if all the work done by the gas was performed within the calorimeter, the cooling, owing to expansion, would be just balanced by the warming of the tubes at the constricted points. Also, a persistent lowering of the values of $L$ would be caused, and (as above pointed out) I now find that such is not the case. To test this matter at the time, however, I observed the
rate of rise due to the "stirring supply"—firstly, when no air was passing; secondly, when the air was passing through the dry flask and tubes and I could detect no difference.

So long as the thermal balance is maintained with the same potential difference, the rate of evaporation must be the same, whatever method is adopted. I cannot see that the external work to be done is likely to alter because the space above the water is de-saturated by passing a gas instead of removing the saturated vapour by an exhaust, and this view is borne out by the close agreement between the means of those groups and my later experiments.

There is one curious fact which may possibly throw some light on the matter. I performed two experiments (August 22 and September 13), passing nitrogen instead of air. Of course I had at that time no means of judging of the comparative value of the different experiments, and therefore was ignorant of the close approximation of the nitrogen values and my final ones. Had I then been aware of the coincidence, I should have continued the nitrogen experiments in order to ascertain if the agreement was fortuitous.

The close agreement is shown in the following table:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Results of nitrogen experiments</th>
<th>Final values</th>
</tr>
</thead>
<tbody>
<tr>
<td>24°96</td>
<td>581-68 (1 cell)</td>
<td>581-73</td>
</tr>
<tr>
<td>89°88</td>
<td>572-72 (2 cells)</td>
<td>572-69</td>
</tr>
</tbody>
</table>

When time allows, I propose to repeat these nitrogen experiments, in the hope that some light may thereby be thrown on the matter; in the meantime, I am unable to suggest any sufficient explanation of this phenomenon.


A study of the results obtained from the experiments described in the last section led me to the conclusion that it was necessary to seek some other method of attacking the problem. I have not described many of the precautions I gradually adopted during those experiments, but since none of them had produced any appreciable improvement it was evident that the real cause of the irregularities had not been ascertained. Even the entire change involved by the replacement of aniline by oil, the removal and refitting of the calorimeter, &c., appeared to have had no effect of any kind.

I determined, therefore, to adopt an alternative method of producing evaporation, viz., by reducing the total pressure below the pressure of the saturated vapour. It
possessed the following great advantages: (1) there would be no necessity for the passage of gas through the apparatus, (2) the weighing-bulbs, &c., for catching the aqueous vapour could be dispensed with. I was, however, reluctant to adopt this method, for I anticipated that several practical difficulties would present themselves; for example, it would be necessary to insert a known weight of water into the flask, and continue the experiments until the whole of that water was evaporated, thus I should not be able to finish the experiment at any time when \( \theta_1 = \theta_0 \), as was the case during the "pressure" experiments.

It would also be more difficult to maintain the thermal balance at such perfection as in the former experiments, for it would be less easy to control the rate of evaporation.

Again, when air was passing through the apparatus, the water in the flask was efficiently stirred and its temperature in consequence approximated closely to that of the calorimeter, even when the rate of evaporation was rapid. A thermometer \( (G_2) \) was, during the preliminary experiments, placed as described in Section V., with its bulb near the bottom of the flask, and I found that the difference in temperature between the flask water and the calorimeter liquid did not, in the greatest case, exceed 0\(^\circ\)15 C. If no gas was passing, the water would not be stirred, and it appeared probable that the difference in temperature might greatly exceed this amount. In this case not only would the observed temperature \( (\theta_1) \) exceed the real temperature of the water, but also the vapour when escaping through the coil would abstract heat from the calorimeter, and thus (as pointed out by Winkelmann in his criticisms of Regnault's experiments) the resulting value of \( L \) would be too great.

It did not appear possible to determine the interior flask temperature accurately by means of a mercury thermometer, whose bulb was placed in a chamber where the pressure was reduced to something between 10 and 100 millims., and if I placed a platinum thermometer in the flask, a third electrical circuit and galvanometer would have had to be added with a third observer to read the indications—additions which circumstances did not render possible.

I did not feel that it would be of any use to adopt Regnault's method of determining the temperature by the vapour pressure (see Section II.), and I endeavoured therefore to find some means of preventing the temperature of the evaporating water from falling below that of the walls of the flask.

It was evident that the smaller the quantity of contained water, the more nearly would its temperature approximate to that of the surface upon which it rested. If it was possible to discharge the water drop by drop on to the silver surface, the difference in temperature would probably be negligible, and after some trials I found a method of effecting this. A glass tube, exactly fitting into the communicating tube \( h h' \) (Plate 5, fig. 1) was closed at one end, the other end being drawn out so that it would pass through the constriction at the calorimeter lid (see p. 279), and the narrow tube which thus projected into the flask, terminated in a very fine opening.
A tube of this kind (which I shall call a "dropper") is shown in place in Plate 5, fig. 1. It was filled with water in the same manner as a "weight thermometer." To ascertained its action, I placed it within a wide glass tube whose lower end was closed. A constriction in the wide tube enabled me to stand the "dropper" within it, so that the narrow portion projected downwards (without touching the bottom) in the same manner as it would do when in situ above the flask. The upper end of the enclosing tube was connected with the exhaust pumps, a clamp being fixed on the connections. I found that when the pressure fell below that of the aqueous vapour, the water in the dropper was discharged into the surrounding chamber in a succession of small drops, but that if the communication with the exhaust was closed the dropping ceased. If the vacuum was maintained, the drops first thrown on the walls disappeared while a fresh supply was ejected. I concluded that when the space was absolutely saturated there was equilibrium, and I found that the disturbance of that equilibrium, caused by an almost imperceptible decrease in the pressure, was sufficient to maintain the flow. The size of the orifice of the dropper did not appear to be of any consequence, as I ascertained by experiment. Of course a certain amount of water-vapour must have been formed to saturate the space left within the dropping tube as the water retreated. It is evident, however, that the quantity thus evaporated would be very small. At the highest temperature at which I have yet worked (50° C.), the specific volume of water-vapour is somewhat below 12,000, and as the volume of the droppers used did not exceed 4·1 cub. centims., the weight of water required to saturate this space would be about 0·001 gram, and at lower temperatures much less. The greater portion of the heat required for such evaporation must, however, have been taken from the calorimeter, for the shoulder of the dropper rested on the metal ring at the base of the tube h h' (Plate 5, fig. 1), and this ring formed a portion of the calorimeter. In order to make certain of this matter, I lowered the filled dropper into place, the contained water being slightly cooler than the calorimeter temperature, and deduced its water equivalent in the manner described in Appendix II., where I show how the capacity for heat of the thermometer (\(G_3\)) was ascertained. The weight of water and glass in the dropper being known, its water-equivalent could also be alternatively obtained by calculation. It was difficult to accurately ascertain the temperature of the dropper just before lowering it into place, but the experimental results were in practical agreement with the calculated ones, and heat which disappeared within the dropper must therefore have been taken from the calorimeter.

It is thus evident that no correction is rendered necessary by this internal evaporation.

The adoption of the exhaust method involved certain changes in the exterior connections. The weighing bulbs and mercury trap were replaced by the bottle B (Plate 6, fig. 1). The connecting tubes which passed into this bottle were ground to fit and no corks were used. The calorimeter exit tube did not dip into the \(\text{H}_2\text{SO}_4\) but terminated about an inch above the surface of the acid. The manometer gave

MDCCCXCV.—A.
(after comparison with the barometer) the pressure of the vapour in the condenser. The tube H branched into two; one was connected with a water pump, by which the pressure could be brought down to about 20 millims., and the other with a Geissler's mercury pump.

_description of an experiment._

The dropper was filled by alternate boiling and cooling, and was allowed to stand in a vessel of warm water until the temperature had fallen to about 5° above that to which it was to be exposed during the experiment. After removal from the water it was thoroughly dried externally and placed in a short glass tube closed at both ends by rubber corks, a precisely similar tube closed in the same manner being used as a tare. The case and dropper when full weighed about 20 grams.

The dropper was always filled some hours before an experiment and placed in the balance case until wanted. After the tank temperature had become steady the dropper and its case, having been weighed, were placed within a larger tube immersed in the tank water.

The connections of the electric circuit having been completed, the calorimeter temperature \( (\theta_1) \) was made coincident with the tank temperature \( (\theta_0) \), the current being then switched on to the alternative coil, and thus (as previously explained) the temperature of the external resistances was kept steady, even when the current was not passing through the calorimeter. The dropper and case were then removed from the tank, a silk thread was passed through a platinum loop, fused into the top of the dropper, and it was lowered into its place at the bottom of the tube \( h \)
(Plate 5, fig. 1). The thread was withdrawn and an air-tight piston, consisting of a section of a rubber cork mounted on a glass rod, was thrust down \( h \) until it arrived at the top of the dropper. A slightly larger conical rubber cork, mounted on the same rod, closed the top of the tube \( h \), therefore all diffusion or evaporation up the connecting tube was prevented, and no difficulty was experienced in closing it in such a manner as to be absolutely air-tight.

It was necessary to delay the commencement of the experiment until the dropper and contained water had assumed the temperature of the calorimeter \( (\theta_1) \). This took some time, although the temperature of the former must (owing to the previous immersion in the tank) have been very nearly \( \theta_1 \). Observation of the thermometer-galvanometer gave the extent of the cooling caused by the introduction of the dropping tube. The current was then switched on until \( \theta_1 \) again equalled \( \theta_0 \), the galvanometer was observed, and the process repeated until no further cooling effect was visible.

It appeared possible that slight evaporation through the fine opening of the dropper might during this interval be the cause of some cooling, and I was for a time very

* I found that it was necessary to fix a small capillary tube within the dropper, otherwise the contained water refused to start boiling when the external pressure was removed.
HEAT OF EVAPORATION OF WATER.

uneasy about this point. I found, however, that if the tube, after filling and weighing, was placed in a desiccator for 12 hours with the opening uncovered, the loss of weight was less than 0.008 gram; it was, therefore, not probable that any appreciable evaporation took place during the interval occupied by the temperature adjustment. Again, the dropper, after being filled, was removed from the beaker at a higher temperature than that of the tank, so that immersion in the calorimeter would not lead to the expulsion of any water, provided that the small air-bubble formed at the lower end when the dropper was cooled in the balance case did not rise into the upper part of the instrument, in which case the re-heating would possibly cause a small expulsion, owing to the warming of the air-bubble, which was previously absent from the tube. I think it just possible that this happened in some of the earlier experiments (Nos. I. to V.), but, after No. V., I adopted a new form of tube, of which the lower end was first turned up for about 1 centim., and then bent at right angles. Thus any air-bubble formed during the cooling remained at the open end, and also the water, when ultimately expelled, was thrown against the side of the flask (see Plate 5, fig. 1).

The results of experiments performed after this alteration are in closer agreement than preceding ones.

When \( \theta_1 \) was found by observation to have become quite steady, the contact-maker of the bridge was carefully adjusted to the bridge null-point (see p. 288), and the swing (if any) of the galvanometer was read. If \( \theta_1 \) was found to be lower than \( \theta_0 \), a further adjustment was made. In cases where \( \theta_1 \) slightly exceeded \( \theta_0 \), no adjustment was possible without again removing the dropper, so, unless the difference was considerable (e.g., a swing exceeding 50 or 60, that is, a difference of about 0.01 C., see Table V., supra), the experiment was proceeded with. Three observations were taken of the swing, and the chronograph tape was marked during the second observation. This gave the commencement of the interval of time \( t_o \), i.e., the time during which the stirring supply had to be estimated.

The pressure in the condenser B had been previously brought down below that required during the experiment, and, immediately after the observer at the galvanometer had registered the swings, the tap T_4 was opened. The manometer M at once showed an increase of pressure, due to the air in the flask and tubes expanding into the condenser. The expansion of this air produced a visible cooling effect, causing a galvanometer swing of about 90—equivalent to nearly 0.02 C. (Table V., supra). The manner in which this loss of heat was compensated for will be described later.

The water pump having been cut off by the tap T_6, the mercury pump was if necessary brought into action. The moment at which the discharge from the dropper commenced was indicated with great accuracy by the galvanometer and announced by Observer No. II. The electric current was at once switched on to the calorimeter circuit (the action recording itself on the chronograph tape) and the electric balance,
if not perfect, immediately adjusted by Observer No. I. Owing to the alternative-circuit method previously described, only a very trifling adjustment was as a rule required. Observer I. had now to direct his attention to the maintenance of the thermal balance. This, as I have anticipated, was found at first to be matter of some difficulty, but practice rendered the task comparatively easy.

The discrepancies observable in the earlier experiments (Table XI.) are, I expect, in some measure due to fluctuations in the value of $\theta_1$. As a general rule, the evaporation at the start was too rapid, the pressure having been too much reduced by the last stroke of the pump—the galvanometer swing amounting to as much as $-500$ or $-600$ (nearly $0^\circ\text{C}$). The tap $T_4$ was closed and (evaporation being thus prevented) the electric current was allowed to raise $\theta_1$ until the + galvanometer swing announced by Observer II. was about equal to the previous negative swing; the time occupied by these two large oscillations being only a minute or two. $T_4$ was then partially opened until it was found that $\theta_1$ was slowly falling. When $\theta_1$ became equal to $\theta_0$ the rate of cooling was further decreased and during the remainder of the experiment the galvanometer swing (which was called aloud by Observer II. every 15 or 20 seconds) rarely exceeded 50 or 60 (i.e., about $0^\circ\cdot01$ C.) and in many cases the difference between $\theta_1$ and $\theta_0$ did not exceed $0^\circ\cdot002$ C. in the course of half-an-hour.

As the whole of the aqueous vapour passing into the condenser was not at once absorbed by the $\text{H}_2\text{SO}_4$, the pressure slowly increased, and thus gave a further power of adjustment. The large bulb of the Geissler was kept vacuous and thus, by opening the tap $T_7$ the pressure in the condenser could at any time be decreased. By one rapid turn of the tap an almost imperceptible rise of the manometer $M$ was caused, and a very slight difference in pressure produced a considerable alteration in the cooling rate; thus, if $\theta_1$ was rising, a single revolution of the tap $T_7$ would check the rise, another revolution would probably give the cooling a slight mastery. The operations by which the thermal balance was maintained may, as I have described them, appear both cumbersome and difficult. I can only say that (after the first three or four experiments) the control was nearly perfect and a single oscillation of as much as $0^\circ\cdot01$ C. would have been considered excessive. From beginning to end of each experiment great care was taken that each positive oscillation should be succeeded by a corresponding negative one.

The electric balance was also maintained by Observer I.; but as the temperature of the coil did not appreciably alter throughout, this balance required but little attention.

The taps $T_4$, $T_b$, $T_7$, and $T_2$, as well as the handles of the rheochord and all the electric keys, were so placed as to be within reach of Observer I. without change of position. The high resistance galvanometer screen was immediately in front of him, and also the manometer, $M$, whose readings were constantly observed. Near the commencement and end of an experiment the physical strain was great, but when both
HEAT OF EVAPORATION OF WATER.

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thermal and electrical balances had been finally adjusted there were often intervals of more than ten minutes when no alterations had to be made.

From beginning to end, the task of Observer II. was that of announcing the galvanometer swings—a monotonous and uninteresting operation, which, however, required constant attention.

When the experiment was approaching its termination a close watch had to be kept, for, unless the current was switched off the instant a sudden rise showed that all the water had been evaporated, the lapse of a few seconds would have raised \( \theta_1 \) considerably above \( \theta_0 \). If, on the other hand, the current was turned off too soon, it was always possible to switch it on again and raise \( \theta_1 \) up to \( \theta_0 \). After the first experiment it was easy to calculate (knowing the weight of the empty and the full dropper) the approximate time of ending. As a rule I cut off the current two or three seconds before that time, then increased the vacuum considerably to make sure of evaporating off the last drop of water, again established the current, and brought \( \theta_1 \) to just below \( \theta_0 \), repeating this process as often as necessary—all the actions recording themselves on the chronograph tape. When \( \theta_1 \) had become absolutely steady, or only showed the slight increase due to the stirring, it was safe to assume that all the water had been evaporated.

The tap \( T_4 \) was then finally closed, the tap \( T_3 \) slowly opened, and the air from the drying bottles \( S \) and \( P \) allowed to pass in through the 30-feet coil, \( C_1 \), in the tank. The increase of \( \theta_1 \) caused by the compression of this air was found, by observation, to be the same as the depression (previously referred to) which took place during exhaustion, and it was to allow for this rise that \( \theta_1 \) was set slightly below \( \theta_0 \). When the internal and external pressures had become equal, \( T_3 \) was closed and the current again switched on if necessary, until the swing became the same as the initial swings. If, however, \( \theta_1 \) exceeded \( \theta_0 \), this was not possible, and a correction had afterwards to be made for any difference.

After repeated observation had shown that \( \theta_1 \) was steady, Observer II. read, as before, three galvanometer swings, pressing his chronograph key at the middle one. This record gave the termination of the interval \( t_s \), the time during which the stirring heat had to be estimated.

It will be seen from the preceding account that \( t_s \) always considerably exceeded \( t_e \), the time of electrical supply.

The plugs closing the tube \( h, h' \) (Plate 5, fig. 1) were now withdrawn, a wire ending in a hook passed down the tube, the dropper extracted by means of its platinum loop, and immediately returned to its case, which was at once corked and placed on the balance, and afterwards weighed, with the various precautions previously referred to.

The only remaining operation was that of translating the chronograph tape which gave the value to \( \frac{1}{10} \) second of \( t_e, t_s \), and the time of each thousand revolutions of the stirrer.

Remarks on Tables XI. to XIII.

Tables XI., XII., and XIII. give the experimental results; Table XI. those at
temperatures approximating to 40°; Table XII. those at temperatures near to 30°; and Table XIII. two experiments at 30°, where the rate of evaporation was but \( \frac{3}{4} \) of the former rate. Any inaccuracy in the values of \( Q_n \), \( t_n \) and \( \Sigma q \) would in these last experiments tell with double force. Also, the rate of evaporation being so greatly diminished, it was probable that any depression of the temperature of the evaporating water below \( \theta_1 \) would be about half of what it was when four cells were used, and thus the magnitude of any error, caused by such depression, would be indicated.

Had time permitted, I should have repeated these experiments with a still slower rate of evaporation. I was, however, surprised to find that it was more difficult to maintain the thermal balance with the lower than with the higher D.P.

A large number of differently shaped and sized "dippers" were used, hence the difference in the values of \( M \).

As I preferred to alter the conditions as much as possible, no effort was made to keep the stirring rate the same for different experiments.

In most cases the droppers when removed after an experiment appeared to be absolutely dry. In two cases, however, some signs of moisture were visible. I am at a loss to account for this, as I feel sure that evaporation had ceased, and that there was no water left on the surface of the silver flask. The moisture thus remaining was, of course, included in the final weighing, and would not therefore introduce any error provided the flask was dry. It is noticeable, however, that the two experiments at the end of which this moisture was visible (Nos. V. and IV.) give, as shown by Table XI. (b), the highest values for \( L \).

The value of \( d' - d'' \) will be noticed as unusually high in No. I. Here we had no idea of the time when the experiment would finish, and did not allow for the rise in \( \theta_1 \) caused by the introduction of the dry air at the end, hence the close of the experiment found \( \theta_1 \) too high by nearly 0°028 C. Also we could only approximate to the value of \( t_n \), having in the hurry of the initial experiment forgotten to mark the time of finish. The remembrance of a casual observation of the clock, however, enabled us to fix it approximately. An error of 100 seconds in \( t_s \) would in that experiment produce an error of not quite \( \pm 25 \) in \( L \), and the value assigned to \( t_s \) is probably within a minute of the truth.

During Experiment II. a portion of the mercury covering the core of tap \( T_3 \) became, owing to careless manipulation, sucked into the apparatus, and in some unexplained manner stopped the evaporation for nearly ten minutes, during which the electric current had to be switched off. However, the accident had but little effect on the resulting value of \( L \).

No. XI. was an almost perfect experiment, the thermal balance being maintained very closely throughout. I do not think that the variations in \( \theta_1 \) during this experiment at any time amounted to 0°005 C., and the external temperature \( (\theta_0) \) remained,

* Even when the same dropper was used, and the bulb was afterwards found to be dry, the values of \( M \) were not identical. The mass of contained water depended on the temperature of the dropper when removed from the beaker after filling, and as the beaker was only roughly brought to a temperature somewhat above \( \theta_1 \), the values of \( M \) varied.
as shown by Col. III., absolutely unchanged. It is noticeable that its result (Table XI. (b)) is almost exactly the mean value of Experiments VI. to XII.

I have included in these tables every experiment performed by the exhaust method with the exception of one, during a portion of which the chronograph ceased to mark, or rather marked continuously. Both accident and its cause were only discovered at the end of the experiment, when it was found that a loose piece of wire had short-circuited the chronograph circuit.

Notation used in Tables XI. to XIII.

Col. I. Number of experiment and date.

II. Temperature of the experiment \( (\theta_0) \) on the nitrogen scale.

III. \( m_1 \) the initial mass of dropper and contents, \( m_2 \) the final mass; hence

\[
M = m_1 - m_2
\]

(\( M \) is in all cases the weight corrected to vacuum.)

IV. Time (in seconds) during which the electric current was passing through the calorimeter \( = t_s \).

V. Time \( t_s \) (in seconds) during which the stirring supply of heat was maintained. \( t_s = \) duration of experiment.

VI. Number of revolutions per second of the stirrer \( = r_1 \).

VII. Difference \( (\theta' - \theta''_0) \) between the initial \( (\theta'_0) \) and final \( (\theta''_0) \) temperature of the surrounding walls. This is expressed in the nitrogen scale, the value of each millimetre of thermometer II. having been previously determined by the comparison referred to in Section IV.

VIII. Let \( \theta'_1 \) (initial calorimeter temperature) exceed \( \theta'_0 \) by \( d' \), and let \( \theta''_1 \) (final calorimeter temperature) exceed \( \theta''_0 \) by \( d'' \).

Then this column gives value of \( d' - d'' \) deduced from the galvanometer swings by Table V., Section VI.

IX. Gives the capacity for heat of calorimeter and contents \( (C) \) at the temperature of the calorimeter \( \theta_1 \) (Table III.).

X. The temperature of the Clark cells during the experiment.

XI. The value of \( R_1 \) at temperature \( \theta_1 \) from Table VII., Section VIII.

XII. The average pressure \( (p'') \) in the condenser during the experiment (in millimetres of Hg).

XIII. The approximate pressure of saturated vapour \( (p') \) at the temperature \( \theta_1 \) (from Regnault's tables).

XIV. The difference between Cols. XIII. and XII. This indicates the limit of fall of pressure from the flask to the condenser, \( i.e., \) along about 19 feet of narrow tubing. It must be remembered that owing to the presence of the \( \text{H}_2\text{SO}_4 \) the pressure in the condenser fell off greatly, and Col. XIII. is only useful as indicating a value considerably exceeding the real difference between \( p' \) and \( p'' \). No use is made of this quantity in the reduction of the observations.
Table XI. (α).—Experimental Results at Temperatures nearly 40° C. Number of Cells in Series* = 4.

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
<th>IX.</th>
<th>X. Temp. cells.</th>
<th>XI. R₁</th>
<th>XII. p'</th>
<th>XIII. p</th>
<th>XIV. p'−p''</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Sept. 17</td>
<td>40.147</td>
<td>3.7852</td>
<td>2866.4</td>
<td>3229.2</td>
<td>5.235</td>
<td>0</td>
<td>−0.376</td>
<td>318</td>
<td>15.12</td>
<td>10.379</td>
<td>46</td>
<td>55</td>
<td>9</td>
</tr>
<tr>
<td>II.</td>
<td>18</td>
<td>40.146</td>
<td>3.7954</td>
<td>2851.8</td>
<td>4077.7</td>
<td>5.266</td>
<td>+0.005</td>
<td>+0.049</td>
<td>318</td>
<td>15.04</td>
<td>10.379</td>
<td>47</td>
<td>55</td>
</tr>
<tr>
<td>III.</td>
<td>18</td>
<td>40.147</td>
<td>3.5039</td>
<td>2635.1</td>
<td>3811.2</td>
<td>5.420</td>
<td>−0.030</td>
<td>+0.037</td>
<td>318</td>
<td>15.18</td>
<td>10.379</td>
<td>47</td>
<td>55</td>
</tr>
<tr>
<td>IV.</td>
<td>19</td>
<td>40.144</td>
<td>3.5240</td>
<td>2648.0</td>
<td>3732.1</td>
<td>5.252</td>
<td>−0.045</td>
<td>+0.012</td>
<td>318</td>
<td>14.96</td>
<td>10.379</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>V.</td>
<td>19</td>
<td>40.145</td>
<td>2.5217</td>
<td>2650.3</td>
<td>3518.4</td>
<td>5.314</td>
<td>−0.055</td>
<td>+0.0163</td>
<td>318</td>
<td>15.14</td>
<td>10.379</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>VI.</td>
<td>20</td>
<td>40.147</td>
<td>3.8558</td>
<td>2899.5</td>
<td>4890.5</td>
<td>5.357</td>
<td>0</td>
<td>−0.108</td>
<td>318</td>
<td>15.04</td>
<td>10.379</td>
<td>47</td>
<td>55</td>
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<tr>
<td>VII.</td>
<td>21</td>
<td>40.147</td>
<td>3.7877</td>
<td>2825.1</td>
<td>3714.0</td>
<td>5.313</td>
<td>−0.005</td>
<td>+0.018</td>
<td>318</td>
<td>14.99</td>
<td>10.379</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>VIII.</td>
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<td>40.147</td>
<td>3.8564</td>
<td>2902.0</td>
<td>3984.3</td>
<td>5.330</td>
<td>−0.040</td>
<td>+0.026</td>
<td>318</td>
<td>15.04</td>
<td>10.379</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>IX.</td>
<td>22</td>
<td>40.149</td>
<td>4.0046</td>
<td>3007.0</td>
<td>4490.6</td>
<td>5.239</td>
<td>−0.0002</td>
<td>+0.012</td>
<td>318</td>
<td>14.92</td>
<td>10.379</td>
<td>47</td>
<td>55</td>
</tr>
<tr>
<td>X.</td>
<td>23</td>
<td>40.157</td>
<td>4.0088</td>
<td>3005.1</td>
<td>4335.1</td>
<td>5.440</td>
<td>−0.0006</td>
<td>+0.0124</td>
<td>318</td>
<td>14.91</td>
<td>10.379</td>
<td>47</td>
<td>55</td>
</tr>
<tr>
<td>XI.</td>
<td>25</td>
<td>40.138</td>
<td>4.0037</td>
<td>3006.0</td>
<td>4229.2</td>
<td>5.307</td>
<td>0</td>
<td>−0.0006</td>
<td>318</td>
<td>13.86</td>
<td>10.379</td>
<td>47</td>
<td>55</td>
</tr>
</tbody>
</table>

* Number of cells actually in use = 16.
### Table XII. (α).—Experimental Results at Temperatures near 30° C. Number of Cells in Series = 4.

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
<th>IX.</th>
<th>X. Temp.</th>
<th>XI.</th>
<th>XII.</th>
<th>XIII.</th>
<th>XIV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number and date.</td>
<td>$\alpha_0$</td>
<td>$m_1 - m_2$</td>
<td>$m_1$</td>
<td>$m_2$</td>
<td>$r_1$</td>
<td>$\delta_0 - \delta_v$</td>
<td>$\delta' - \delta''$</td>
<td>$C_{\delta_v}$</td>
<td>cells.</td>
<td>$R_{c_v}$</td>
<td>$p''$</td>
<td>$p'$</td>
<td>$p' - p''$</td>
</tr>
<tr>
<td>XII. Oct. 4</td>
<td>29.987</td>
<td>4.0017</td>
<td>3.0228</td>
<td>3.4515</td>
<td>5.314</td>
<td>0</td>
<td>-0.0123</td>
<td>312</td>
<td>15.92</td>
<td>10.354</td>
<td>23</td>
<td>31</td>
<td>8</td>
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<tr>
<td>XIII.</td>
<td>6</td>
<td>29.983</td>
<td>3.9894</td>
<td>3.0073</td>
<td>4.3634</td>
<td>5.411</td>
<td>-0.0015</td>
<td>0</td>
<td>312</td>
<td>14.86</td>
<td>10.354</td>
<td>24</td>
<td>31</td>
</tr>
<tr>
<td>XIV.</td>
<td>6</td>
<td>29.998</td>
<td>3.9872</td>
<td>3.0075</td>
<td>4.5323</td>
<td>5.386</td>
<td>0</td>
<td>-0.0040</td>
<td>312</td>
<td>14.96</td>
<td>10.354</td>
<td>23</td>
<td>31</td>
</tr>
<tr>
<td>XV.</td>
<td>6</td>
<td>29.999</td>
<td>3.9919</td>
<td>3.0103</td>
<td>4.6280</td>
<td>5.294</td>
<td>+0.0010</td>
<td>+0.0020</td>
<td>312</td>
<td>14.32</td>
<td>10.354</td>
<td>23</td>
<td>31</td>
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<tr>
<td>XVI.</td>
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<td>30.004</td>
<td>4.2015</td>
<td>3.1699</td>
<td>5.0037</td>
<td>5.195</td>
<td>-0.0020</td>
<td>+0.0035</td>
<td>312</td>
<td>14.96</td>
<td>10.354</td>
<td>24</td>
<td>31</td>
</tr>
</tbody>
</table>

### Table XIII. (α).—Results near 30° C. Number of Cells in Series = 3.

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
<th>IX.</th>
<th>X. Temp.</th>
<th>XI.</th>
<th>XII.</th>
<th>XIII.</th>
<th>XIV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number and date.</td>
<td>$\alpha_0$</td>
<td>$m_1 - m_2$</td>
<td>$m_1$</td>
<td>$m_2$</td>
<td>$r_1$</td>
<td>$\delta_0 - \delta_v$</td>
<td>$\delta' - \delta''$</td>
<td>$C_{\delta_v}$</td>
<td>cells.</td>
<td>$R_{c_v}$</td>
<td>$p''$</td>
<td>$p'$</td>
<td>$p' - p''$</td>
</tr>
<tr>
<td>XVII.* Oct. 12</td>
<td>29.993</td>
<td>3.0879</td>
<td>4.1008</td>
<td>5.6910</td>
<td>5.257</td>
<td>-0.0010</td>
<td>+0.0066</td>
<td>312</td>
<td>14.96</td>
<td>10.352</td>
<td>25</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>XVIII.</td>
<td>13</td>
<td>29.993</td>
<td>3.0910</td>
<td>4.1166</td>
<td>5.4313</td>
<td>5.425</td>
<td>-0.0005</td>
<td>-0.0049</td>
<td>312</td>
<td>14.92</td>
<td>10.352</td>
<td>26</td>
<td>31</td>
</tr>
</tbody>
</table>

* The potential difference at the ends of the coil was uncertain during the first minute or so of this experiment, owing to a false contact in the Clark cell circuit. After rectifying the mistake it was found that the previous approximate adjustment of the rheochord had made the D.P. slightly too low, and thus $t_r$ is too long, but not by as much as a second, for the error in D.P. during this interval (which certainly did not amount to two minutes) was less than E500, as shown by the movement given to the rheochord.

† The chronograph tape showed that for some unknown reason the stirring rate suddenly altered at about 3000 seconds from the start. Thus the stirring correction has to be applied in two portions.
Reduction of the Observations given in Tables XI. (a) to XIII. (a).

(See Tables XII. (b) to XIII. (b.).)

Col. XV. gives the value of \( Q \delta t = \frac{(ne)^2 \times t_0}{R_1 \times J} \).

The correction for temperature of the cells was made by Lord Rayleigh's coefficient (0.00077), but, as an inspection of Col. X. (supra) will show, the correction was in every case very small, except in XI. During the night of September 25 the Clark cell tank regulator ceased to work, and I found the cells at a temperature of 13° the next morning. I considered it better to keep them at that temperature throughout the day than to raise it to 15° a few hours before an experiment. The correction in this case amounts to 1 in 1500, but is probably accurate to 1 in 5000.

In a communication to the Royal Society, on November 22, 1894, Professor Schuster pointed out an error in my determination of the value of \( J \), viz., that I had not made a necessary correction for the specific heat of the air displaced by the water, for the method I adopted gave the difference in the rate of rise when a certain space was filled first with air and then with water. This correction raises my value of \( J \) by 1 in 4000. Hence, in the following reductions I assume \( J = 4.199 \) in place of 4.198.* As I have before pointed out, if in consequence of errors in my standards, &c., my value of \( J \) is inaccurate, it is still the right value to insert here, where I use the same standards, for errors of the kind referred to are thus eliminated.

Col. XVI. The value of \( Q_s \) as deduced from Col. VI. by means of Table VI., Section VII. (supra).

,, XVII. The "stirring supply" \( Q_{ds} \) from Cols. XVI. and V.

,, XVIII. The term \( \Sigma q = C_0 \left\{ \left( \theta'_0 - \theta''_0 \right) - \left( d' - d'' \right) \right\} \) from Cols. VII., VIII., and IX.

,, XIX. Gives the sum of Cols. XV., XVII., and XVIII., that is, the total number of thermal grams used in evaporating the mass \( M \) (Col. III.).

,, XX. Repeats the value of \( \theta_0 \), in order to render the reference less troublesome.

,, XXI. The value of \( L \), deduced from the equation \( L = \frac{Q_{ds} + Q_{ds} + \Sigma q}{M} \).

* This correction should not be applied to the values of the specific heat of aniline given in Paper A. In that case the results also depended on the observations of differences, and if the corrected value of \( J \) was there used, a further correction for the specific heat of the air displaced by the aniline would have to be made, the final values remaining practically unaltered.
HEAT OF EVAPORATION OP WATER.
Table XI.

(b).

—Eeduction of the Observations

XV.
QeU

Experiment.

XVII.

XVIII.

XIX.

Q

QA.

2g.

2.

I.

21640

00443

II.

2152-1
1987-3
1999-5
2000-9

•00454
•00509
•00449
•00471

VI.
VII.
VIII.

2189-1
2133-4

IX.
X.
XI.

2271-7
2269-7

•00486
•00546
•00480
•00452
•00517
•00468

III.

rv.
v.

21910

22736

Table XII.

(b).

—Reduction

XV.

Experiment.

2288-5
2277-2
2276-9
2279-3
2400-1

XII.

xni.
XIV.

XV.
XVI.

in Table XI. (a),

XVI.
s-

XVI.

XVII.
XVIII.

XV
\

n

'

XXI.
L.

.

40 ? 147

57311

40-146

40-144
40-145

572-31
572-77
572-61
573-80

23-8
20-3

-3-4

2209-5

+ 3-3

21570

191

-0-4

20-3
22-7

-o-i

193

-0-2

2209-7
2291-9
2293-5
2292-7

40-147
40-147
40-147
40-149
40-157
40-133

573-01
572-50
573-00
572-28
572-12
572-61

40-146

572-74

40-147

572-59

+ 1-1

Mean

of all

Mean

of Nos. VI. to

XL

.

.

40147

.

of the Observations in Table XII. (a),

XVII.

00614

30-7

•00644
•00696

O

2169-5
2172-3
2006-9
2018-1
2020-9

316
32-1

307

XVII.

36-7

36 7

=

4.)

XIX.

XX.

XXI.

2$.

2.

e

L.

-3-8
-0-5
-1-3

+ 0-9
+ 0-2

.

2308-3
2307-7
2310-9
2431-0

29 ?987
29-983
29-998
29-999
30-004

578-58
578-64
578-78
578-90
578-60

....

29-994

578-70

23151

(n

=

3.)

XVIII.

XIX.

XX.

XXI.

23

2.

e

L.

.

-o-i
-1-7

Mean
2 s 2

(n

XVIII.

of the Observations in Table XIII. (a),

,

1750-1
1753-4

XX.

4.)

+ 1-7
+ 0-2
+ 1-8
+ 3-4

30-4

XVI.

=

-8-8

Mean

Experiment.

(n

14-3
18-5
19-4
16-8
16-6

•00672
•00723
•00710
•00663

Table XIII. (b).— Eeduction

315

.

1786-7
1788-4

29 ?993
29-993

578-83
578-60

....

29-993

578-72


I have already remarked that I attach more value to Experiments VI. to XI. than to the preceding ones, and I shall therefore assume the mean value of $L$ at $40^\circ$·15 as 572·60.

The close agreement between the means of Nos. XII. to XVI. and Nos. XVII. and XVIII. is very satisfactory when it is remembered that the rate of evaporation is in the last case nearly halved.

I need scarcely say that, had time permitted, I should have performed more experiments, especially at $30^\circ$. I do not, however, consider that the evidence would have been greatly strengthened.

In the whole of the series from VI. onwards (i.e., after the adoption of the bent form of dropper) there is no experiment which gives results differing from the mean at that temperature by more than 1 in 1430, and in the groups at $30^\circ$ the greatest divergence is 1 in 2900. The probable mean error of a small group of experimental results of this kind is therefore less than the probable error of some of the constants on which our conclusions are based, and a larger accumulation of such experimental numbers would not necessarily bring us any nearer to the absolute value.

**Conclusions.**

<table>
<thead>
<tr>
<th>Temperature, Nitrogen thermometer.</th>
<th>Value of $L$ (in terms of thermal unit at $15^\circ$ C.).</th>
</tr>
</thead>
<tbody>
<tr>
<td>$40^\circ$·15 C.</td>
<td>572·60</td>
</tr>
<tr>
<td>$30^\circ$·00 C.</td>
<td>578·70</td>
</tr>
</tbody>
</table>

**Section XI.—Discussion of the Results.**

From the conclusions arrived at in the last section we obtain (over the range $30^\circ$ to $40^\circ$·15 C.) $dL/d\theta = -0010$.

Suppose we assume with Regnault that $L$ is a linear function of $\theta$, it follows that

- when $\theta = 0^\circ$, $L = 596·73$
- when $\theta = 100^\circ$, $L = 336·63$

I admit the folly of attempting to extrapolate to such an extent where we have no evidence but that given by the experiments themselves. It is a different matter when we can bring forward independent evidence.

In Section II. I dwelt upon the importance of the experiments of Dieterici at low, and of Regnault at high temperatures; the agreement between the values obtained by those observers and the ones resulting from the above extrapolation is so extraordinary that I give in detail their experimental numbers.

As stated in Table I., ante, the mean value of all Dieterici's experiments was 596·8 at $0^\circ$. He, however, regards certain of the experiments (whose results are given in his Tables II. and IV.) as of greater value than others, because the evaporating water was included in a platinum instead of a glass tube, and thus its
temperature must have approximated more nearly to the external temperature. His numbers are as follows (‘Wied. Ann.,’ vol. 37, 1889, pp. 502-4):

Table XIV.—Dieterici’s Experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature</th>
<th>“Total heat.”</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>99.49</td>
<td>638.8</td>
</tr>
<tr>
<td>8</td>
<td>99.46</td>
<td>636.3</td>
</tr>
<tr>
<td>9</td>
<td>99.31</td>
<td>636.4</td>
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<td>99.28</td>
<td>637.6</td>
</tr>
<tr>
<td>11</td>
<td>100.31</td>
<td>636.0</td>
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<td>100.19</td>
<td>636.8</td>
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<td>100.19</td>
<td>638.3</td>
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<td>637.9</td>
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<td>635.9</td>
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<td>17</td>
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<td>637.9</td>
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<td>637.9</td>
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<tr>
<td>19</td>
<td>100.26</td>
<td>635.6</td>
</tr>
<tr>
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<td>100.26</td>
<td>635.8</td>
</tr>
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<td>21</td>
<td>100.26</td>
<td>636.7</td>
</tr>
<tr>
<td>22</td>
<td>100.22</td>
<td>637.6</td>
</tr>
<tr>
<td>23</td>
<td>100.22</td>
<td>638.4</td>
</tr>
<tr>
<td>24</td>
<td>100.22</td>
<td>636.8</td>
</tr>
<tr>
<td>25</td>
<td>100.22</td>
<td>636.6</td>
</tr>
</tbody>
</table>

Table IV. . . . { 597.07 (with lower pressure) 596.63

Mean of all experiments in platinum tubes . . . 596.73

His own summary of these results is as follows:—

"Die Versuche mit dem Plattingefasse ergeben

\[ r = 596.73 \]

mit einem wahrscheinlichen Fehler des Mittels von \( \pm 0.13 \)."

Regnault performed forty-four experiments at temperatures about 100\°. Of these he rejects Nos. 1 to 6, as merely preliminary; the remainder are as follows. It should be remembered that the numbers in this table give the values of the "total heat," not those of L.

Table XV.—Regnault’s Experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature</th>
<th>“Total heat.”</th>
<th>Experiment</th>
<th>Temperature</th>
<th>“Total heat.”</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>99.49</td>
<td>638.8</td>
<td>26</td>
<td>100.22</td>
<td>637.2</td>
</tr>
<tr>
<td>8</td>
<td>99.46</td>
<td>636.3</td>
<td>27</td>
<td>100.37</td>
<td>636.1</td>
</tr>
<tr>
<td>9</td>
<td>99.31</td>
<td>636.4</td>
<td>28</td>
<td>100.32</td>
<td>636.1</td>
</tr>
<tr>
<td>10</td>
<td>99.28</td>
<td>637.6</td>
<td>29</td>
<td>100.32</td>
<td>637.3</td>
</tr>
<tr>
<td>11</td>
<td>100.31</td>
<td>636.0</td>
<td>30</td>
<td>100.31</td>
<td>636.1</td>
</tr>
<tr>
<td>12</td>
<td>100.19</td>
<td>636.8</td>
<td>31</td>
<td>100.22</td>
<td>635.6</td>
</tr>
<tr>
<td>13</td>
<td>100.19</td>
<td>638.3</td>
<td>32</td>
<td>100.22</td>
<td>636.9</td>
</tr>
<tr>
<td>14</td>
<td>100.19</td>
<td>637.9</td>
<td>33</td>
<td>100.26</td>
<td>635.9</td>
</tr>
<tr>
<td>15</td>
<td>100.19</td>
<td>635.9</td>
<td>34</td>
<td>100.26</td>
<td>635.7</td>
</tr>
<tr>
<td>16</td>
<td>100.26</td>
<td>635.9</td>
<td>35</td>
<td>99.09</td>
<td>636.1</td>
</tr>
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<td>100.26</td>
<td>637.9</td>
<td>36</td>
<td>99.09</td>
<td>636.1</td>
</tr>
<tr>
<td>18</td>
<td>100.26</td>
<td>637.9</td>
<td>37</td>
<td>99.07</td>
<td>636.6</td>
</tr>
<tr>
<td>19</td>
<td>100.26</td>
<td>635.6</td>
<td>38</td>
<td>99.07</td>
<td>636.9</td>
</tr>
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<td>20</td>
<td>100.26</td>
<td>635.8</td>
<td>39</td>
<td>99.36</td>
<td>636.1</td>
</tr>
<tr>
<td>21</td>
<td>100.26</td>
<td>636.7</td>
<td>40</td>
<td>99.36</td>
<td>636.8</td>
</tr>
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<td>22</td>
<td>100.22</td>
<td>637.6</td>
<td>41</td>
<td>99.33</td>
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<td>23</td>
<td>100.22</td>
<td>638.4</td>
<td>42</td>
<td>99.33</td>
<td>636.4</td>
</tr>
<tr>
<td>24</td>
<td>100.22</td>
<td>636.8</td>
<td>43</td>
<td>99.27</td>
<td>635.7</td>
</tr>
<tr>
<td>25</td>
<td>100.22</td>
<td>636.6</td>
<td>44</td>
<td>99.27</td>
<td>636.8</td>
</tr>
</tbody>
</table>

Mean . . . 99.88 636.67

MR. E. H. GRIFFITHS ON THE LATENT

This value of 636.67 at 99°-88 would become 636.60 at 100°. If we assume that 1 gram of water gives out 100 thermal units in cooling from 100° to 0°, we get

\[ L = 536.60 \text{ at } 100°. \]

**Values of L.**

<table>
<thead>
<tr>
<th></th>
<th>0°</th>
<th>100°</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regnault</strong></td>
<td>596.73</td>
<td>536.60</td>
</tr>
<tr>
<td><strong>Dieterici</strong></td>
<td>596.73</td>
<td>536.63</td>
</tr>
<tr>
<td><strong>Griffiths (extrapolated)</strong></td>
<td>596.73</td>
<td>536.63</td>
</tr>
</tbody>
</table>

I have learned to regard experimental coincidences with suspicion, they are so often misleading, but such an unusual case as the above merits attention.

These coincidences are the more extraordinary on account of the following considerations.

Dieterici assumed (ante, p. 265) as his thermal unit the "mean thermal unit" from 0° to 100° C. Now according to Regnault* the ratio of the "mean thermal unit" to the thermal unit at 0° is as 1.005 to 1.

If we assume Rowland's or Bartoli and Stracciati's determinations of the changes below 15° (my own have not extended below that temperature) we should get

\[ \text{"mean thermal unit" } / \text{thermal unit at } 15° = \frac{1.005}{0.994} \approx \text{approximately}, \]

\[ i.e., \frac{1.011}{1} \]

and thus Dieterici's value of L, if expressed in terms of the same thermal unit as I have used, would be increased to 603.3.

Again, according to Regnault we ought to subtract 100.5 from 636.60 in order to obtain the value of L at 100. This would give \( L = 536.1 \).

Some further considerations, however, tend to show that the agreement at both ends of the line given by my observations is not merely fortuitous. We can deduce the values of L resulting from my "exhaust" experiments (at any temperature \( \theta \)) by the formula,

\[ L = 596.73 - 6010 \theta \ldots (G_1). \]

Now the preliminary experiments (see Table IX., ante) although irregular, carry some weight and the mean of each group is in fair agreement with formula \( (G_1) \).

I have given in Section II. my reasons for rejecting Regnault's experiments at low temperatures, where he determined the temperature in the calorimeter from the pressure of the vapour in the condenser. The objections there brought forward, however, lost all force as regards these experiments above 63° in which the methods of observation and experiment were altered.

Column III. of the following table gives the results of all Regnault's experiments above 63° and below 100° ... (R), Column IV. gives the values resulting from Regnault's own formula \( 606:5 + 305t \ldots \) (R), Column V. contains those given by Winkelmann's formula* ... (W), which includes Regnault's expression for the capacity for heat of water, and Column VI. the numbers obtained by assuming the validity of formula \( G_1 \) (supra), from which we deduce

\[
\text{Total Heat} = 596.73 + 3990\theta \ldots \ (G_2).
\]

Column VII. gives the difference between (R) and (R), in Column VIII. are given the differences between (R) and (W), and Column IX. shows the differences between (R) and (G).

\[
* \quad L = 589.5 - 0.2972t - 0.0082147t^2 + 0.0000008147t^3.
\]
Table XVII.—Comparison between Regnault's Experimental Results \( (R_x) \) over the Range 63° to 88°, with the value given by formulae \( (R), (W), \) and \( (G_3) \).

<table>
<thead>
<tr>
<th>I. No. of experiment</th>
<th>II. Temperature ( (R_x) )</th>
<th>III. Experimental results ( (R_x) )</th>
<th>IV. ( (R) )</th>
<th>V. ( (W) )</th>
<th>VI. ( (G_3) )</th>
<th>VII. ( (R_x)-(R) )</th>
<th>VIII. ( (R_x)-(W) )</th>
<th>IX. ( (R_x)-(G_3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88.11</td>
<td>633.4</td>
<td>633.4</td>
<td>632.4</td>
<td>631.9</td>
<td>0</td>
<td>+0.9</td>
<td>+1.5</td>
</tr>
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<td>2</td>
<td>87.83</td>
<td>633.1</td>
<td>633.2</td>
<td>632.3</td>
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<td>-0.1</td>
<td>+0.8</td>
<td>+1.3</td>
</tr>
<tr>
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<td>632.7</td>
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<td>-2.6</td>
</tr>
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<td>85.24</td>
<td>628.6</td>
<td>632.5</td>
<td>631.5</td>
<td>630.7</td>
<td>-3.2</td>
<td>-2.9</td>
<td>-2.1</td>
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<td>630.7</td>
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<td>+0.2</td>
<td>+1.0</td>
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<td>630.5</td>
<td>-0.8</td>
<td>-1.3</td>
<td>-0.6</td>
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<td>630.7</td>
<td>629.9</td>
<td>-2.9</td>
<td>-1.8</td>
<td>-1.0</td>
</tr>
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<td>82.66</td>
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<td>631.7</td>
<td>630.6</td>
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<td>+1.3</td>
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<td>81.03</td>
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<td>628.9</td>
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<td>-0.3</td>
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<td>10</td>
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<td>+0.7</td>
<td>+1.6</td>
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<td>78.26</td>
<td>627.0</td>
<td>630.3</td>
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<td>628.0</td>
<td>-3.3</td>
<td>+2.0</td>
<td>-1.0</td>
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<td>76.50</td>
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<td>629.8</td>
<td>628.3</td>
<td>627.2</td>
<td>-1.2</td>
<td>+0.3</td>
<td>+1.4</td>
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<td>628.2</td>
<td>624.4</td>
<td>625.2</td>
<td>-3.8</td>
<td>+2.0</td>
<td>-0.8</td>
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<td>71.11</td>
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<td>628.1</td>
<td>626.3</td>
<td>625.1</td>
<td>-5.9</td>
<td>-4.1</td>
<td>-2.9</td>
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<td>628.0</td>
<td>626.1</td>
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<td>+0.8</td>
<td>+2.0</td>
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<td>627.7</td>
<td>625.7</td>
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<td>-4.8</td>
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<td>-1.4</td>
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<td>626.7</td>
<td>624.5</td>
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<td>+0.2</td>
<td>+1.5</td>
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<tr>
<td>22</td>
<td>64.34</td>
<td>629.9</td>
<td>626.1</td>
<td>623.9</td>
<td>622.4</td>
<td>-3.2</td>
<td>-1.0</td>
<td>+0.5</td>
</tr>
<tr>
<td>23</td>
<td>63.02</td>
<td>625.5</td>
<td>625.7</td>
<td>623.2</td>
<td>621.9</td>
<td>-0.2</td>
<td>+2.3</td>
<td>+3.6</td>
</tr>
</tbody>
</table>

Sum of differences ... -49.3 -17.6 +5.2
Mean difference ... -2.14 -0.77 +0.23

If we omit Experiment 23, we get
Sum of differences ... -49.1 -19.9 +1.6
Mean difference ... -2.23 -0.90 +0.07

The results of the above comparison show that over the range 63° to 88° the formula \( (G_3) \) gives a closer approximation to Regnault's experimental numbers than either of the other formulae. The only reasonable explanation of these various coincidences which occurs to me is that the value of the "mean thermal unit" is practically the same as the value of the "thermal unit at 15° C."*

* Further evidence can be adduced in support of this view. In Section II. I pointed out that if we express the results of the observations of Bunsen and Regnault, on the latent heat of fusion of
I see nothing impossible in this supposition. As stated in Section II. there is sufficient evidence that at low temperatures the capacity for heat decreases with rise of temperature. Rowland found a minimum indicated near 34°. If therefore the capacity for heat increases gradually above some such temperature, but more rapidly near 100°, it is quite conceivable that the "mean thermal unit" should closely approximate to the "thermal unit at 15° C." Our only experimental evidence to the contrary is that given by Regnault in his paper, "De la Chaleur Spécifique." We know that his conclusions at low temperatures are incorrect, and I do not see that those at higher temperatures have greater value, for his methods of observation and experiment were, in this case, unaltered.

The matter, of course, can only be cleared up by a direct determination of the capacity for heat of water over the range 0° to 100°.

In the meantime I contend that the evidence in favour of the formula "total heat = 596·73 + 3990 \( \theta \)" is stronger than that upon which either Regnault's or Winkelman's formulae are based.

At temperatures above 100° the values of "the total heat" deduced by formula \((G_2)\) would be higher than Regnault's experimental numbers. The capacity for heat of water at higher temperatures is so uncertain, and it has so great an influence on the values of \(L\) at high temperatures when deduced from the "total heat" formula, that I do not feel that a discussion on these results would at present be of any value.

The results of the experimental work described in preceding sections, and of the evidence brought forward in this section, may be summarised as follows:

The values obtained by Dieterici at 0°, by Regnault at temperatures 63° to 100° C., and by Griffiths at intermediate temperatures are (assuming the approximate equality of the "mean thermal unit" and the thermal unit at 15° C.) closely represented by the formula

\[
L = 596·73 - 0·6010\theta.
\]

[Note, May 7, 1895.—The suggestion that the "mean thermal unit" does not exceed the "thermal unit at 15° C." has been criticized as over bold. It is, therefore, with peculiar pleasure that I include in this paper a communication which I have to-day received from Dr. Joly, to whom I return my sincere thanks for his permission to publish it.

Dr. Joly informs me that he regards his experiments as preliminary; their importance, however, is undoubtedly great. They are (I believe) the first experiments since those of Regnault which throw any light on the relative values of the two units. It will be seen that (assuming Bartoli and Stracciati's conclusions as to the changes in the capacity for heat of water from 0° to 15° C.) the results of Dr. Joly's experiments indicate that the ratio

ice in terms of the same unit, by means of the ordinarily accepted comparison of the values of their respective thermal units, their difference becomes excessive.

MDCCXCV.—A.
Mean thermal unit
Thermal unit at 15° C. = 9952 = 0.9957
1
in place of \( \frac{1.011}{1} \).

It is apparent that there is sufficient evidence to justify scepticism as to the validity of the commonly accepted ratio, and I hope that the demonstration of this uncertainty may quicken further investigation into the actual value of this important constant.

Note (by Dr. J. Joly, F.R.S.) on the Ratio of the Latent Heat of Steam to the Specific Heat of Water.

Upon receiving from Mr. Griffiths a copy of the abstract of his paper on the latent heat of steam, I determined upon making some experiments with the steam calorimeter on the ratio of the latent heat of steam to the mean specific heat of water over the range air temperature 12° to 100°. Pending the completion of a form of the calorimeter which will enable me to make this comparison over suitable and definite ranges of temperature, I gladly add, at Mr. Griffiths' request, the following note on the experiments already made.

The weight of water operated upon was 12.8545 grms. This was enclosed in a thin blown glass bulb, sealed while the water was boiling, and having an internal volume of 15.714 cub. centims. Ten experiments were made—these were in close agreement. The mean initial temperature was 11°-89; the mean steam temperature 99°-96. The first temperature was determined by a Kew-corrected thermometer reading tenths on an open scale; the second temperature determined by a standard barometer. The mean weight of steam condensed was 2.32917 grms.

To correct this for the effect of the glass vessel, six experiments were made on the latter when containing dry air only. Further corrections were made \((a)\) for evaporation within the vessel when containing water; \((b)\) for buoyancy or displacement effect on the apparent weight of the vessel, the densities being not quite the same in the experiments on the filled and empty vessel; \((c)\) for the specific heat of the air contained in the vessel when empty of water. A total subtractive correction of 0.2298 grm. was obtained.

If we now calculate the mean specific heat of water between 11°-89 and 99°-96, assuming the value of the latent heat of steam given by Mr. Griffiths' formula, \(i.e.,\)

\[
L = 596.73 - 0.6010 \theta, \text{ where } \theta \text{ has the value } 99°-96, \text{ we get}
\]

\[
C = \frac{20994 \times 536.66}{12.8545 \times 88.07} = 0.99520.
\]

I have little doubt that this will remain—closely—the mean specific heat, 12°-100°, according to the steam calorimeter. It will, of course, be necessary to check the result by further experiments. It is true I formerly made experiments in the steam
calorimeter and obtained a higher value, but it was in an early and very defective form of the instrument, and an error of positive sign, as I afterwards found, very certainly obtained in those experiments.

Considering this number in the light of Mr. Griffiths' remarks, it certainly supports his contention that Regnault made an error of excess in his value of the mean calorie—0° to 100°. The above number is however, even less than the value supposed by Mr. Griffiths to be the true number. For, as I understand, Mr. Griffiths' L is calculated on the calorie at 15° C. as unity. If this is also—as Mr. Griffiths suggests as probable—in close agreement with the mean calorie, 0° to 100°, then the mean specific heat from 12 to 100 should come out only a very little less than unity. In fact, by plotting Bartoli and Stracciati's observations below 15°, we can estimate what the mean specific heat from 12° to 100° ought to be if the mean from 0 to 100 is the same as the specific heat at 15° and both equal unity. A rough estimate gives this to be 0.9995.

My value is therefore too low to be in harmony with the supposition that the mean calorie and the 15° unit are identical. The value of the latent heat of steam is, of course, involved, for the steam calorimeter can only give a ratio, and, if the number now obtained is correct, it follows that either the latent heat assumed is too low, or the specific heat of water is even lower than it is supposed to be, or possibly both are somewhat incorrect.

J. Joly.

Physical Laboratory,
Trinity College, Dublin.]

Section XII.—The Density and Specific Volume of Saturated Water-vapour deduced by means of the Thermodynamic Equation from the Values of L given by Formula (G₁).

Winkelmann (as previously stated) assigns to what he terms the "theoretical density" of water-vapour the value 0.6225 (air = 1). He gives, however, no information regarding the data for this statement.

The most recent investigation of the comparative volumes in which oxygen and hydrogen combine is that by Scott, whose conclusions are as follows:* "That 100,000 volumes of oxygen unite with 200,245 volumes of hydrogen to form water. Applying this to the density of oxygen found by Lord Rayleigh to be 15.882, we get for the atomic weight of oxygen 15.862."

In close agreement with this conclusion we have---

Dittmar . . . . . . . . 15.866
Cooke and Richards . . . . 15.869

* 'Phil. Trans.,' A, 1893, p. 567. Also 'Science Progress,' August, 1894.
Assuming Scott and Rayleigh's values we get—

Molecular weight of water-vapour = 17.862.

Lord Rayleigh in 1888–9* pointed out that Regnault's conclusions as to the weights of unit volumes of hydrogen and air required correction, as Regnault had not allowed for the change in volume of the bulb consequent on changes in pressure. Crafts† has applied this correction, and finds the resulting comparative densities of air and hydrogen to be as follows:

<table>
<thead>
<tr>
<th></th>
<th>Regnault's value.</th>
<th>Corrected value.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1</td>
<td>1.06926</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>1.06949</td>
</tr>
</tbody>
</table>

Ostwald‡ deduces from these numbers the weights of 1 litre at 0° and 76 centims., as

Air, 1.29349 grams. Hydrogen, 0.08988 gram.

Hence we get

"Theoretical Density" of water-vapour = 0.6206 (air = 1).

I will now proceed to deduce the density at various temperatures by means of the thermodynamic equation

\[ L = \frac{T}{J} \left( s' - s \right) \frac{dp}{dT}, \]

and I assume the values of the various quantities to be as follows:

\[ J = 4.199 \times 10^7. \] (My value after Schuster's correction for the specific heat of the displaced air, see p. 314, supra).

\[ L = 596.73 - 6010 \theta \] . . . formula G (supra).

\[ T = 273.7 + \theta. \]

The values of \( \frac{dp}{dT} \) are taken from Broch's reduction of Regnault's experimental results,§ and are as follows:

---

† 'Comptes Rendus,' vol. 106, pp. 1662-4, 1888.
HEAT OF EVAPORATION OF WATER.

Table XVIII.

<table>
<thead>
<tr>
<th>I.</th>
<th>II. $\frac{dp}{dT}$ (millim. of Hg).</th>
<th>III. $\frac{dp}{dT}$ (dynes per sq. centim.).</th>
<th>IV. $p$ (millim. of Hg).</th>
</tr>
</thead>
<tbody>
<tr>
<td>e.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.330</td>
<td>4401.1</td>
<td>4.569</td>
</tr>
<tr>
<td>20</td>
<td>1.073</td>
<td>14368</td>
<td>17.363</td>
</tr>
<tr>
<td>40</td>
<td>2.366</td>
<td>39150</td>
<td>54.865</td>
</tr>
<tr>
<td>60</td>
<td>6.922</td>
<td>92301</td>
<td>148.89</td>
</tr>
<tr>
<td>80</td>
<td>14.388</td>
<td>191850</td>
<td>354.87</td>
</tr>
<tr>
<td>100</td>
<td>26.981</td>
<td>359800</td>
<td>760</td>
</tr>
</tbody>
</table>

The numbers in Column III. are obtained by assuming $g = 980.94$ and density of mercury = 13.596.

The resulting values of $s'$ (specific volume) and $d$ (density, air = 1) are given in the following table:

Table XIX.

<table>
<thead>
<tr>
<th>I. Temperature.</th>
<th>II. $s'$.</th>
<th>III. Specific volume of air.</th>
<th>IV. $d$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>207970</td>
<td>128600</td>
<td>6184</td>
</tr>
<tr>
<td>20</td>
<td>55430</td>
<td>36318</td>
<td>6215</td>
</tr>
<tr>
<td>40</td>
<td>19581</td>
<td>12278</td>
<td>6270</td>
</tr>
<tr>
<td>60</td>
<td>7644</td>
<td>4814</td>
<td>6298</td>
</tr>
<tr>
<td>80</td>
<td>3395.6</td>
<td>2141</td>
<td>6305</td>
</tr>
<tr>
<td>100</td>
<td>1676.9</td>
<td>1056.2</td>
<td>6299</td>
</tr>
</tbody>
</table>

The specific volume of air was calculated by the formula

$$\frac{1}{0.0012935} \times \frac{(273.0 + \theta)}{273.0} \times \frac{760}{p} = 2152.2 \times \frac{273.0 + \theta}{p}.$$

The value of $\frac{dp}{dT}$ at low temperatures is not known with sufficient precision to enable us to attach any weight to the resulting values of $d$. For example, if we take $\frac{dp}{dT} = 0.331$ millim. at 0° instead of 0.330 millim., we get $d = 6204$ in place of 6184. At temperatures above 20° or 30°, not only is the value of $\frac{dp}{dT}$ known with greater certainty, but the effect of any small error is diminished.

A comparison of the "Theoretical Density" (6206) with the numbers in Column IV. of the last table, indicates that aqueous vapour at low pressures approximates in density to that of a perfect gas, but that, at higher pressures, its density exceeds that of a perfect gas.

Above a pressure of about 140 millims., it appears to attain a practically constant density about 1.015 times that of the "theoretical" one.
I have previously pointed out that the values of $L$ given by my experiments are independent of errors in the electrical standards used during my determination of $J$. This, however, is not the case when the density is obtained from the thermo-dynamic equation, as the results then depend upon the absolute value assigned to the mechanical equivalent. Now my corrected value of $J$ exceeds Professor Schuster and Mr. Gannon's by about 1 in 1000, hence the values of $d$ in Col. IV., Table XIX., would, according to Schuster, have to be increased by 0.0006, whereas if we use Rowland's value (4.190) the increase would be about 0.0012.

I have given the above determination of the relative densities of water-vapour and air, because it was the method of calculation adopted by Winkelmann, and therefore enables a comparison to be made between his conclusions and those arrived at by the use of formula $G_1$ (supra). It appears to me to be an unsatisfactory method, as it involves unnecessary data regarding air. A more direct way of obtaining some information concerning the density of water-vapour, is that of finding $PV$, i.e., the "volume energy." Now $PV = RT$, and the value of $R$ for a true gas is 0.0815,* when $P$ is pressure in atmospheres, and $V$ the volume in litres occupied by the molecular weight in grams. Assuming as before the molecular weight of water to be 17.862, and obtaining the values of $V$ and $P$ from Col. II., Table XIX., and Col. IV., Table XVIII., we get:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\frac{PV}{T} = R.$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\circ$</td>
<td>0.0827</td>
</tr>
<tr>
<td>20</td>
<td>0.0823</td>
</tr>
<tr>
<td>40</td>
<td>0.0816</td>
</tr>
<tr>
<td>60</td>
<td>0.0812</td>
</tr>
<tr>
<td>80</td>
<td>0.0811</td>
</tr>
<tr>
<td>100</td>
<td>0.0812</td>
</tr>
</tbody>
</table>

and here again we find that at temperatures near $0^\circ$ water-vapour resembles a true gas.

* This value of $R$ depends on the assumptions that 1 litre of hydrogen at $0^\circ$ and 76 centims. weighs 0.08988 gram. (supra), and that the coefficient of expansion of hydrogen = 0.0036613 (the value obtained by CalleNDAR and myself in 1893). Dr. Shields, however, assigns to $R$ the value 0.0819 (see 'Science Progress,' December, 1894).
Appendix I.—Details of Stirring Experiments when the Calorimeter was Filled with Oil.

The tank temperature having become steady (at \( \theta_0 \)), the calorimeter was raised to a temperature \( \theta_1 \), slightly below \( \theta_0 \). In order that the conditions should become steady, the stirring was allowed to proceed for half-an-hour to one hour, before observations were commenced. The battery key (\( k_3 \), Plate 6, fig. 2) was kept continually oscillating and, as the temperature rose, the swings of the galvanometer diminished, until no motion was observed on reversing the battery circuit. The observer then pressed a key communicating with the chronograph, and thus the time was recorded. As before stated, the stirrer automatically registered its own revolutions. At the same moment that the observer at the galvanometer pressed his recording key,* a second observer took the readings on the mercury thermometer, which gave the temperature of the steel walls.

As any change in the mercury thermometer was of great importance, this observation was made with the micrometer eye-piece before referred to.

Groups of five observations were taken about certain previously fixed bridge-wire readings, and each group of five was meaned to find the time of passing the given points.

The following Table gives full particulars of a stirring experiment. It is by no means a good one, but I give it simply because it is the first one done after the introduction of the oil. The exterior temperature was unusually unsteady.

* In the slower experiments, however, instead of using the chronograph, I called the transit, and my assistant recorded the time, as also the time of the revolutions, the stirrer ringing a bell at each 1000.
Table XX.—Stirring experiment No. I., September 17. Temperature of bridge-wire = 64°2 F.

<table>
<thead>
<tr>
<th>Bridge-wire reading</th>
<th>Time of transit</th>
<th>Reading thermometer II</th>
<th>No. of revolutions</th>
<th>Time of revolutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P.M.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>589.8</td>
<td>9 45 16</td>
<td>882.40</td>
<td>0</td>
<td>9 47 36</td>
</tr>
<tr>
<td>590.2</td>
<td>9 45 48</td>
<td>882.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>590.6</td>
<td>9 52 58</td>
<td>882.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>591.0</td>
<td>9 56 58</td>
<td>882.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>591.4</td>
<td>9 59 49</td>
<td>882.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Means . 590.6</td>
<td>9 52 46</td>
<td>882.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9000</td>
<td>10 15 55</td>
</tr>
<tr>
<td>594.2</td>
<td>10 20 11</td>
<td>882.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>594.6</td>
<td>10 24 39</td>
<td>882.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>595.0</td>
<td>10 23 34</td>
<td>882.41</td>
<td>14000</td>
<td>10 31 39</td>
</tr>
<tr>
<td>595.4</td>
<td>10 32 20</td>
<td>882.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>595.8</td>
<td>10 36 36</td>
<td>882.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Means . 595.0</td>
<td>10 28 40</td>
<td>882.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27000</td>
<td>11 12 30</td>
</tr>
<tr>
<td>598.7</td>
<td>11 3 30</td>
<td>882.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>599.1</td>
<td>11 6 58</td>
<td>882.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>599.5</td>
<td>11 11 0</td>
<td>882.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>599.9</td>
<td>11 14 4</td>
<td>882.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600.3</td>
<td>11 18 30</td>
<td>882.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Means . 599.5</td>
<td>11 10 42</td>
<td>882.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39000</td>
<td>11 50 15</td>
</tr>
<tr>
<td>602.9</td>
<td>11 48 28</td>
<td>882.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>603.3</td>
<td>11 51 52</td>
<td>882.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>603.7</td>
<td>11 56 54</td>
<td>882.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>604.1</td>
<td>12 1 44</td>
<td>882.39</td>
<td>42000</td>
<td>11 59 42</td>
</tr>
<tr>
<td>604.5</td>
<td>12 6 12</td>
<td>882.40</td>
<td>45000</td>
<td>12 9 9</td>
</tr>
<tr>
<td>Means . 603.7</td>
<td>11 57 2</td>
<td>882.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean time per 1000 = 188.73
Hence, rate per 1 sec. = 5.299

882.41, No. II., = 40°143 C., and 1 millim. of No. II. at 882 = 0501° C.
1 millim. of bridge-wire (temperature 15°) at 40°1 = 009410° C., therefore,
1 millim. of No. II. = 5.51 millims. of bridge-wire.

The times of transit may appear, and no doubt are, very irregular. It must be remembered, however, that the rise in temperature between the individual observations in each group was not so much as 0°004 C. As this rise took about four minutes, it is evident that the time of transit of so slow a movement cannot be accu-
HEAT OF EVAPORATION OF WATER.

rately determined, but observational errors of this kind are precisely those where a close approximation is secured by taking the mean of a group. If the middle observation of each group is compared with the mean, it is evident that an individual observation might be in error by as much as 20 seconds (the greatest difference in the above table is 12 seconds), but it is improbable that the mean is in error by more than 5 seconds. The example given is the one which had the slowest rate of rise, and hence the discrepancies are more marked than would otherwise be the case. As the total time of the experiment was about 2 hours 20 minutes, an error of even 10 seconds in the mean of each group would affect the result by but 1 in 800, and as an error of 1 in 50 in the value of \( Q \), would only affect my final values of \( L \) by 1 in 5000, the above order of accuracy was more than sufficient.

I will now give the reduction of the observation in the above table.

**Reduction of Stirring Experiment No. I.**

<table>
<thead>
<tr>
<th>Bridge-wire range.</th>
<th>Time ((t'))</th>
<th>Change in thermometer II</th>
<th>Resulting change in range</th>
<th>( d\theta_1/\partial t )</th>
<th>Correction to mean bridge-wire</th>
<th>Correction for temperature bridge-wire</th>
<th>( d\theta_1/\partial t ) corrected.</th>
</tr>
</thead>
<tbody>
<tr>
<td>590.6-595.0</td>
<td>2154</td>
<td>+0.02</td>
<td>+1.11</td>
<td>-0.02094</td>
<td>-0.4</td>
<td>+1.7</td>
<td>-0.02000</td>
</tr>
<tr>
<td>595.0-599.5</td>
<td>2528</td>
<td>-0.014</td>
<td>-0.07</td>
<td>-0.01753</td>
<td>-1.2</td>
<td>+1.5</td>
<td>-0.01753</td>
</tr>
<tr>
<td>599.5-603.7</td>
<td>2772</td>
<td>-0.030</td>
<td>-0.17</td>
<td>-0.01454</td>
<td>+4.3</td>
<td>+1.2</td>
<td>-0.00140</td>
</tr>
</tbody>
</table>

Since \( A \), \( B \), and \( C \) should, if the exterior temperature (No. II.) had not changed, fall on a straight line, the most probable path is obtained by taking \( \frac{1}{3}(2A + B) \) and \( \frac{1}{3}(B + 2C) \) as the rate of rise at the corresponding bridge-wire readings, hence we get

<table>
<thead>
<tr>
<th>Bridge-wire</th>
<th>( d\theta_1/dt )</th>
</tr>
</thead>
<tbody>
<tr>
<td>594.28</td>
<td>-0.001978</td>
</tr>
<tr>
<td>600.15</td>
<td>-0.001558</td>
</tr>
</tbody>
</table>

Now the bridge-wire null-point = 598.35 + 0.03\( \theta_1 \) (see p. 288). Therefore null-point at 40° = 599.55. We can now deduce the value of \( d\theta_1/dt \) at this null-point. We get 0.001600.

Hence

\[
(d\theta_1/dt)_r = 0.001600,
\]

when \( r_1 = 5.299 \) and \( \theta_1 \) is measured in millims. of the bridge-wire scale.

I think that there is no necessity to give details of the remaining experiments; MDCCXCV.—A.
the following table shows the results of all those experiments at different rates where $\theta_0 = 40^\circ 1$ approximately.

**Table XXI.**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Date</th>
<th>$(d\theta_1/dt)_s$</th>
<th>$r$</th>
<th>$tr\times 10^{-1}$</th>
<th>$tr^2 \times 10^{-2}$</th>
<th>$tr^3 \times 10^{-3}$</th>
<th>$tr^4 \times 10^{-3}$</th>
<th>From formula $A.$ (infra)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Sept. 17</td>
<td>0.001600</td>
<td>5.299</td>
<td>331</td>
<td>176</td>
<td>930</td>
<td>492</td>
<td>0.001606</td>
</tr>
<tr>
<td>IX.</td>
<td>Oct. 27</td>
<td>0.001626</td>
<td>5.310</td>
<td>327</td>
<td>173</td>
<td>921</td>
<td>489</td>
<td>0.001619</td>
</tr>
<tr>
<td>VI.</td>
<td>Oct. 7</td>
<td>0.001733</td>
<td>5.456</td>
<td>304</td>
<td>166</td>
<td>906</td>
<td>494</td>
<td>0.001805</td>
</tr>
<tr>
<td>II.</td>
<td>Sept. 23</td>
<td>0.002152</td>
<td>5.070</td>
<td>263</td>
<td>149</td>
<td>847</td>
<td>480</td>
<td>0.002104</td>
</tr>
<tr>
<td>III.</td>
<td>Oct. 24</td>
<td>0.002152</td>
<td>7.890</td>
<td>97</td>
<td>76</td>
<td>605</td>
<td>478</td>
<td>0.007930</td>
</tr>
</tbody>
</table>

Experiments II. and III. were only performed with the object of ascertaining the effect of changes of rate. Although the differences between $tr^4$ may appear considerable, it must be remembered that this constant was only required in order to reduce experiments at different rates to some standard rate; in reality, when we consider that we are dealing with the fourth power of $r$ the uniformity is remarkable.

If we plot the values of $(d\theta_1/dt)_s$ obtained from the formula

$$
(d\theta_1/dt)_s = \frac{r^4}{491000}, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (A),
$$

the results are in close agreement with the experimental ones, especially when the rate is between 5.2 and 5.5 (the extreme limits of rate during the Latent Heat experiments, the usual value being about 5.3). True, if we assume $(d\theta_1/dt)_s = r^2/92000$ our results would be nearly as close over the above limited range, but Experiments II. and III. indicate that the true relation is more nearly given by the previous expression. In any case, the difference between the experiments and the results as deduced from (A) do not differ by 1 in 100 over the above range of rate, and a difference of 1 in 100 in $Q$, would only cause a difference of about 1 in 10,000 in $L$.

**Table XXII.—** The experiments at $30^\circ$ give the following results.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Date</th>
<th>$(d\theta_1/dt)_s$</th>
<th>$r$</th>
<th>$tr^2 \times 10^{-2}$</th>
<th>$tr^3 \times 10^{-3}$</th>
<th>$tr^4 \times 10^{-3}$</th>
<th>From formula $B$ (infra)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.</td>
<td>Sept. 29</td>
<td>0.002330</td>
<td>5.280</td>
<td>629</td>
<td>333</td>
<td>333</td>
<td>0.002314</td>
</tr>
<tr>
<td>VIII.</td>
<td>Oct. 27</td>
<td>0.002380</td>
<td>5.320</td>
<td>632</td>
<td>337</td>
<td>337</td>
<td>0.002383</td>
</tr>
<tr>
<td>VII.</td>
<td>Oct. 7</td>
<td>0.002568</td>
<td>5.416</td>
<td>619</td>
<td>335</td>
<td>335</td>
<td>0.002560</td>
</tr>
<tr>
<td>V.</td>
<td>Oct. 7</td>
<td>0.005973</td>
<td>6.750</td>
<td>515</td>
<td>348</td>
<td>348</td>
<td>0.006178</td>
</tr>
</tbody>
</table>
If we assume
\[ tr^4 = 336000, \]
we get
\[ \left( \frac{d\theta_1}{dt} \right)_e = \frac{r^4}{336000} \] (B).

And here again the differences between the experiments and the results from (B) are much below 1 per cent. at rates between 5·2 and 5·5, and again the experiment at higher speeds (Expt. V.) indicates that \( tr^4 \) is more constant than \( tr^3 \).

Applying formulae (A) and (B), we can deduce the rise for a rate of 5·300.

Values of \( (d\theta_1/dt)_e \), at rate 5·300:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( (d\theta_1/dt)_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>40·1</td>
<td>0·001608</td>
</tr>
<tr>
<td>30·0</td>
<td>0·002348</td>
</tr>
</tbody>
</table>

Now (see Appendix II, Experiment IV.) it was found that when a similar experiment was performed at 40°·1, where the heat supply was that due to a potential difference of three Clark cells at 15° together with a stirring supply (at rate 5·277), then

\[ (d\theta_1/dt)_e = 1·4853 \text{ (mean bridge-wire millim.)}. \]

Now (from A) we get

\[ (d\theta_1/dt)_e = 0·00158 \text{ at rate 5·277}, \]
therefore \( (d\theta_1/dt)_e = 1·4695 \), therefore

\[ (d\theta_1/dt)_e = \frac{1·4695}{9} = 0·1633, \]

hence

\[ \frac{(d\theta_1/dt)_e}{(d\theta_1/dt)_e} = \frac{161}{1633} \text{ at rate 5·300 (supra) = 0·0986.} \]

Now the corrected resistance at this temperature (Table VIII.) was 10·376 ohms where the D.P. was that of one Clark cell, and since

\[ H = \frac{e^2}{R_1 \times J} \text{ per sec., we have } \frac{1·4342^2}{10·376 \times 4·198} = 0·04723 \text{ thermal gram,} \]
therefore

\[ Q_e \text{ (rate 5·300) = 0·04723 \times 0·0986 = 0·004659 thermal gram.} \]

\[ 2 + 2 \]
In the same manner (Appendix II., Experiments V. and VI.) it was found that at temperature 30° 

\[(d\theta_1/dt)_{50} = 15035, \quad \text{and} \quad (d\theta_1/dt)_{40} = 002348 \quad \text{(formula B, supra)},\]

hence 

\[
\frac{(d\theta_1/dt)_{50}}{(d\theta_1/dt)_{40}} = \frac{234.8}{1671} = 0.1405,
\]

and at 30° 

\[R_1 = 10.348,\]

therefore 

\[H = \frac{1.4342^2}{10.348 \times 4.198} = 0.04735 \text{ thermal gram per sec.}\]

therefore 

\[Q_s (\text{rate } 5.300) = 0.04735 \times 1.405 = 0.06654 \text{ thermal gram.}\]

Now assuming (A) and (B), it follows that \(r^4/Q_s\) is constant, and we can deduce that if \(r_1\) be any rate and 5.300 the standard rate

At temp. 40°, \(Q_s = 0.04659 + (r_1^4 - 789) \times 0.0000059 \ldots \]  \[\text{(C)}.\]

At temp. 30°, \(Q_s = 0.006654 + (r_1^4 - 789) \times 0.0000084 \ldots \]  \[\text{(D)}.\]

I performed one stirring experiment at 50° and two at 20° and I give the results only, as the values of \(Q_s\) at these temperatures are not required for the reduction of the L experiments described in this paper. I was unable (for want of time) to prove how nearly the effect of changes of rate could be expressed in the same manner as at 30° and 40°, but as the rate was nearly 5.3, the corrections introduced by the reduction to rate 5.3 were very small. The results were of use, as on plotting the curve for the values of \(Q_s\) at the four different temperatures it showed no signs of irregularity, and thus gave additional strength to the determinations at 30° and 40°. The values are as follows:

At temp. 50°, \(Q_s = 0.00235 + (r_1^4 - 789) \times 0.0000030 \ldots \) \[\text{(E)}.\]

At temp. 20°, \(Q_s = 0.00768 + (r_1^4 - 789) \times 0.0000098 \ldots \) \[\text{(F)}.\]

The values of \(Q_s\) at 30° and 40° receive a certain amount of support from the preliminary experiments referred to in Section VII. Although my results by that method varied considerably amongst themselves, the mean of five experiments at 40° gave 0.00000802 gram of water evaporated per 1 sec. by the stirring after reduction to rate 5.3, and the mean of four experiments at 30° gave 0.0001187 gram of \(\text{H}_2\text{O}\) evaporated per sec. at the same rate.
Now, if we assume \( L \) at 40° = 573 and \( L \) at 30° = 579, we can deduce the values of \( Q_s \), which are as follows:

\[
\begin{align*}
\text{At 40°, } Q_s &= 0.00460 \\
\text{at 30°, } Q_s &= 0.00658.
\end{align*}
\]

These results differ from those obtained without any weighing or passing of air (equations C and D supra) by 1 in 77 and 1 in 94 respectively. As an order of accuracy of 1 in 50 was sufficient for my purpose, I considered this independent evidence valuable, although I believe the former method to be by far the most exact.

I also performed a determination of \( Q_s \) at 50° by an evaporating experiment. This gave 0.0000521 gram per sec. Assuming \( L = 567 \), this would give \( Q_s = 0.00295 \), far too high a value as compared with that given by equation (E). This evaporation experiment was a very unsatisfactory one, however, and I attach but little importance to it—in any case, the doubt would not affect the values of \( L \).

To conclude this portion of the subject, I admit that it would have been advisable to perform more of these stirring experiments at 30° and 40°, but at the same time, I think the evidence is sufficient to warrant the assumption that the values of \( Q_s \) cannot be in error by as much as 1 in 50 and are probably correct to better than 1 in 100.

Appendix II.—Details of the Experiments by which the Capacity for Heat of the Calorimeter and Contents was ascertained.

The temperature of the calorimeter was adjusted in the same manner as that described in Appendix I.

The time of transit across five bridge-wire divisions about the readings 50, 60, and 70 centims. was taken, and the times at 50, 60, and 70 deduced. I give particulars of Experiment IV., as that was the one quoted in Appendix I, from which the value of \( Q_s \) at 40.1 was deduced.
Table XXIII.—Experiment No. IV., September 17.

Number of Clark cells 3 (each consisting of 4 in 11). Temperature cells, $15^\circ-14$ C.; temperature bridge-wire, $63^\circ-5$ Fahr.

<table>
<thead>
<tr>
<th>Bridge-wire reading</th>
<th>Time (chronograph)</th>
<th>Revolutions (1000's)</th>
<th>Time</th>
<th>External temperature by thermometer II.</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>81.7</td>
<td>0</td>
<td>100.1</td>
<td>882.35</td>
</tr>
<tr>
<td>49.5</td>
<td>113.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>144.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>176.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>207.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>144.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>730.5</td>
<td>3</td>
<td>639.0</td>
<td>882.40</td>
</tr>
<tr>
<td>59.5</td>
<td>764.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>797.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.5</td>
<td>831.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>865.6</td>
<td>4</td>
<td>858.5</td>
<td>882.40</td>
</tr>
<tr>
<td></td>
<td>797.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>1421.0</td>
<td>7</td>
<td>1426.6</td>
<td>882.40</td>
</tr>
<tr>
<td>69.5</td>
<td>1456.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1493.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.5</td>
<td>1529.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>1565.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1493.1</td>
<td>Time per 1000</td>
<td>189.50</td>
<td>882.40</td>
</tr>
</tbody>
</table>

The operations necessary for the reduction of Experiment IV. are as follows:—

Data required.

Mean value of 1 centim. of range in terms of mean bridge-wire centim. (given by calibration of bridge-wire; see p. 285)—

- 50 to 60 . . . . . . . . 1.00082
- 60 to 70 . . . . . . . . . .99551.

Correction for temperature bridge-wire to $15^\circ$ C. = range $\{1 + 0.0016 (F.° - 59)\}$

* Fuller particulars concerning this method of reduction will be found in Paper A.
HEAT OF EVAPORATION OF WATER.

1 millim. of No. II. = 5'51 millims. of bridge-wire, and 882'40 millims. = 40°'142.
Bridge-wire null-point = 599'55 millims.

<table>
<thead>
<tr>
<th>Range</th>
<th>Time over range</th>
<th>Change temperature on therm. II.</th>
<th>Resulting change range</th>
<th>( \frac{d\theta_1}{dt} \times 10^4 )</th>
<th>Correction to mean bridge-wire ( \times 10^4 )</th>
<th>Correction for temperature C. cells and bridge-wire ( \times 10^4 )</th>
<th>Corrected ( \frac{d\theta_1}{dt} ) ( \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>centims.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 to 60</td>
<td>652'0</td>
<td>+0'3</td>
<td>16</td>
<td>1539'9</td>
<td>+1'3</td>
<td>-0'4</td>
<td>1536'7</td>
</tr>
<tr>
<td>60 to 70</td>
<td>695'3</td>
<td>0</td>
<td>0</td>
<td>1438'1</td>
<td>4'1</td>
<td>0'0</td>
<td>1433'0</td>
</tr>
</tbody>
</table>

Hence we get 1'5367 and 1'4330 as the values of \( \frac{d\theta_1}{dt} \)\(_{50} \) at 55 and 65 centims. respectively. We can thus deduce the value at the null-point (599'55). We get 1'4853.

Now (Appendix I) the value of \( \frac{d\theta_1}{dt} \)\(_{50} \) for rate 5'277 = 0'0158, therefore \( \frac{d\theta_1}{dt} \)\(_{50} \) = 1'4695.

Now \( \frac{d\theta_1}{dt} \)\(_{50} \) \( \times \frac{R_1 \times C_b}{(ne)^2} \) gives the rise per second in degrees C. with unit resistance and unit potential difference, where \( R_1 \) is the resistance in true ohms of the coil at temperature \( \theta_1 \), \( n \) the number of Clark cells of P.D. \( e \) volts, and \( C_b \) the value of the mean bridge-wire millim. at 15° C. when \( \theta_1 = 40^\circ \cdot 1 \), expressed in terms of the N thermometer (see p. 289). Hence if \( T \) is the time of rising 1° C., we get

\[
T = \frac{(ne)^2}{(\frac{d\theta_1}{dt})_e \times R_1 \times C_b},
\]

and

\[
R_{50} = 10'377 \text{ (see Table VIII.}, \ (ne)^2 = 18'513, \text{ and } C_b = 0'09100,
\]

therefore

\[
T = 1334'1,
\]

and

\[
C_{\theta_1} = \frac{T}{J} \text{ (where } C_{\theta_1} \text{ is capacity for heat at } \theta_1), \text{ and } J = 4'199,
\]

therefore

\[
C_{\theta_1} = 317'82 \text{ thermal grams.}
\]

The following table gives the results of all the experiments made with the object of obtaining the values of \( C_{\theta_1} \).
Table XXIV.—Determination of the Capacity for Heat of Calorimeter and Contents.

<table>
<thead>
<tr>
<th>No. of Exp. and date</th>
<th>Mean bridge-wire reading</th>
<th>( \left( \frac{\partial Q}{\partial t} \right)_{m} \times 10^{4} )</th>
<th>Temp. C.</th>
<th>( \left( \frac{\partial Q}{\partial t} \right)_{a} ) at N.P. \times 10^{6}</th>
<th>Stirring rate</th>
<th>( \left( \frac{\partial Q}{\partial t} \right)_{s} )</th>
<th>( \left( \frac{\partial Q}{\partial t} \right)_{a} )</th>
<th>( R_{m} ) (App. III.)</th>
<th>( \phi c \times 10^{6} )</th>
<th>( \frac{T}{J} = \frac{1}{C} )</th>
<th>( \frac{\partial Q}{\partial t} ) \times R_{1} \times C_{b}</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>III. Sept. 10</td>
<td>55</td>
<td>1492.9</td>
<td>50.024</td>
<td>1441.2</td>
<td>5.688</td>
<td>-11.6x</td>
<td>0.014362</td>
<td>10.408</td>
<td>18.513</td>
<td>9128</td>
<td>1363.3</td>
<td>324.74</td>
</tr>
<tr>
<td>II. Sept. 10</td>
<td>65</td>
<td>1389.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV. Sept. 17</td>
<td>55</td>
<td>1534.5</td>
<td>40.122</td>
<td>1482.9</td>
<td>5.742</td>
<td>-22.2</td>
<td>0.014607</td>
<td>10.378</td>
<td>18.513</td>
<td>9100</td>
<td>1342.1</td>
<td>319.74†</td>
</tr>
<tr>
<td>I. Sept. 10</td>
<td>55</td>
<td>1536.7</td>
<td>40.142</td>
<td>1485.3</td>
<td>5.277</td>
<td>-15.8</td>
<td>0.014635</td>
<td>10.377</td>
<td>18.513</td>
<td>9100</td>
<td>1334.1</td>
<td>317.88</td>
</tr>
<tr>
<td>V. Oct. 5</td>
<td>55</td>
<td>1540.6</td>
<td>31.996</td>
<td>1516.1</td>
<td>5.534</td>
<td>-26.2x</td>
<td>0.014899</td>
<td>10.356</td>
<td>18.513</td>
<td>9078</td>
<td>1321.9</td>
<td>314.87†</td>
</tr>
<tr>
<td>VI. Oct. 5</td>
<td>65</td>
<td>1477.3</td>
<td>29.979</td>
<td>1527.2</td>
<td>5.328</td>
<td>-24.0</td>
<td>0.015032</td>
<td>10.351</td>
<td>18.513</td>
<td>9073</td>
<td>1311.5</td>
<td>312.41</td>
</tr>
<tr>
<td>VII. Oct. 21</td>
<td>55</td>
<td>1575.7</td>
<td>29.998</td>
<td>1530.7</td>
<td>5.489</td>
<td>-27.0</td>
<td>0.015037</td>
<td>10.351</td>
<td>18.513</td>
<td>9073</td>
<td>1311.1</td>
<td>312.35†</td>
</tr>
</tbody>
</table>

* The value of \( \frac{\partial Q}{\partial t} \) in Experiments III. and VII. is somewhat doubtful, although it is probably accurate to 1 in 50 (see Appendix I).

† The capacity for heat of the calorimeter during Experiments I, II., and III. was greater by 16 than during the remaining experiments.

‡ The value of \( \frac{\partial Q}{\partial t} \) in Experiment I. is taken from the curve through the values at the other temperatures. I made no direct stirring experiments at 32°.
HEAT OF EVAPORATION OF WATER.

In Paper A. I have given a full account of the determination of the "water equivalent" \( W_1 \) of this calorimeter, and I have every confidence in the values there given.

From Table VI. of that Paper I extract the following:

\[
\begin{array}{cc}
\theta_1 & W_1 \\
20 & 80.11 \\
30 & 80.90 \\
40 & 82.19 \\
50 & 83.39 \\
\end{array}
\]

During these experiments, the silver flask contained a mercury thermometer \( (G_2) \) which was used, during my earlier L experiments, to indicate the internal temperature of the flask. As described (ante), a metal conical tube had been cast on to the stem of this thermometer by means of the alloy, and the tube carefully ground into the neck of the flask to prevent any diffusion of vapour up the glass tube, down which the thermometer passed. After I adopted the "exhaust" method of performing the L experiments, this thermometer was removed from the apparatus; this occurred between Experiments III. and IV., Table XXIV. I had forgotten the circumstance, and when I reduced the results, I was much troubled as to the different values of \( C_n \) given by Experiments II. and IV., which were at about the same temperature. It was some time before the cause of the discrepancy suggested itself to me. I then obtained an approximation to the capacity for heat of thermometer \( G_2 \) and tube, as follows: The temperature of both calorimeter and tank being steady, the bridge was adjusted until the galvanometer ceased to swing. Thermometer \( G_2 \) was then suspended above the tube communicating with the flask, and its temperature read by the reading microscope. It was then rapidly lowered into its place, and observed until its temperature became steady (this took place in about 4 to 5 minutes). The tank being at 40° and the external temperature about 20°, the thermometer rise was about 20°, and a small error in reading was of little consequence. The bridge contact-maker was then re-adjusted, and the change in temperature of the calorimeter deduced from the difference in the readings. Hence the capacity for heat of \( G_2 \) could be found. Four experiments were performed with the following results:

\[
\begin{array}{c}
(1) & 1.52 \\
(2) & 1.65 \\
(3) & 1.62 \\
(4) & 1.58 \\
\hline
\text{Mean} & . & 1.59 \\
\end{array}
\]

MDCCCXCV.—A. 2 x
If we assume the capacity as 1-6, we cannot be greatly in error, and this quantity must be subtracted from the values of \( W_1 \) (supra) for all experiments after No. 3. Now the values of \( C_p \) from Experiments II. and IV. differ by 1-89. This apparent difference of 3 in the results has, however, to be further diminished. On September 14, I found it necessary to withdraw thermometer AB from the calorimeter. Before doing so, I weighed "weighing bottle" containing a roll of blotting-paper, and on removing the thermometer, I wiped its stem and bulb with this paper in order to find the weight of oil withdrawn, which proved to be 104 gram. Hence the differences in Column VI. of the next Table.

**Table XXV.—Specific Heat of Oil.**

<table>
<thead>
<tr>
<th>I. Experiment</th>
<th>II. Temperature</th>
<th>III. ( C_p ) (Table XXIV.)</th>
<th>IV. ( W_1 ) (supra)</th>
<th>V. Cap. of oil</th>
<th>VI. Wt. of oil (vacuo)</th>
<th>VII. ( s_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.</td>
<td>50-024</td>
<td>324-74</td>
<td>83-39</td>
<td>241-35</td>
<td>474-12</td>
<td>50090</td>
</tr>
<tr>
<td>II.</td>
<td>40-122</td>
<td>319-74</td>
<td>82-20</td>
<td>237-54</td>
<td>474-12</td>
<td>5008</td>
</tr>
<tr>
<td>IV.</td>
<td>40-142</td>
<td>317-88</td>
<td>80-60°</td>
<td>237-28</td>
<td>474-02+</td>
<td>4903</td>
</tr>
<tr>
<td>V.</td>
<td>31-096</td>
<td>314-87</td>
<td>81-14</td>
<td>233-73</td>
<td>474-12</td>
<td>4917</td>
</tr>
<tr>
<td>VI.</td>
<td>29-979</td>
<td>312-41</td>
<td>79-30°</td>
<td>233-11</td>
<td>474-02+</td>
<td>4916</td>
</tr>
<tr>
<td>VII.</td>
<td>29-998</td>
<td>312-35</td>
<td>78-51°</td>
<td>228-99</td>
<td>474-02+</td>
<td>4830</td>
</tr>
</tbody>
</table>

Appendix III.—Details of Determination of \( R_1 \).  

In Paper J., p. 409, is given a table showing the errors of all the individual coils in my dial resistance box. These errors were, by kind permission of Mr. Glazebrook, ascertained by direct comparison with the B.A. standards.

I extract the following from the remarks on that table (p. 410, ibid.):

"A table was constructed giving the total difference between the reading and the real value (in terms of "legal ohms") for every position of the plugs in each dial. This difference we termed the "plug correction." Having made this correction, we had then to correct for any inaccuracy in the ratio arms of the bridge, and as all determinations of the calorimeter coil resistance were made with 1000 (right) and 10 (left) as the arms, it is only necessary to here give the correction for those coils.

\[
10L/1000R = 9'9977/1000'30 = 0'0099947.\]

* After removal of thermometer \( G_3 \).
† After removal of 10 gram oil.
‡ The correction for the temperature of the coils was made before applying the "plug correction."
§ There is here a mistake in Paper J. This was corrected in a subsequent communication, 'Proc. Roy. Soc.,' vol. 55, p. 25.
"This we termed the "bridge correction."

"The resulting values are expressed in legal ohms, and true ohms = reading in legal ohms (1 — 0.0024275)."

The above extract is sufficient to explain the operations. I now give a complete example of a determination of \( R_1 \) and the subsequent calculations.

The value of \( \theta_0 \) we obtained by direct observation of thermometer II., and \( d' \) by observation of the bridge reading. Then \( \theta_1 = \theta_0 + d' \).

**Table XXVI.—Determination of Coil Resistance. October 11.**

<table>
<thead>
<tr>
<th>See p. 296.</th>
<th>Galvanometer swings.*</th>
<th>Observed R.</th>
<th>Temperature coils.</th>
<th>( R + r )</th>
<th>Correction for temperature coils.</th>
<th>Plug correction.</th>
<th>( R + r ) (box ohms).</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_1 )</td>
<td>331 170 191 341 140 171</td>
<td>58(\frac{4}{8}) 15</td>
<td>...</td>
<td>58(\frac{4}{5})</td>
<td>+0.02</td>
<td>+0.07</td>
<td>58(\frac{4}{5})</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>417 296 222 350 195 54</td>
<td>1095(\frac{4}{5}) (17^\circ-08)</td>
<td>1095(\frac{7}{8}3)</td>
<td>+0.03</td>
<td>+777</td>
<td>1096(\frac{5}{8}3)</td>
<td></td>
</tr>
<tr>
<td>( N_3 )</td>
<td>407 281 201 322 206 41</td>
<td>1095(\frac{0}{8}3) (12^\circ-61)</td>
<td>1095(\frac{6}{8}4)</td>
<td>+0.03</td>
<td>+777</td>
<td>1096(\frac{6}{8}4)</td>
<td></td>
</tr>
<tr>
<td>( N_4 )</td>
<td>282 128 173 329 109 201</td>
<td>58(\frac{4}{8}3) (15^\circ-29)</td>
<td>...</td>
<td>58(\frac{4}{8}3)</td>
<td>+0.02</td>
<td>+0.07</td>
<td>58(\frac{4}{8}3)</td>
</tr>
</tbody>
</table>

As previously remarked, the difference in the resistance of the leads accounts for the difference between \( N_2 \) and \( N_3 \), and \( N_1 \) and \( N_4 \).

We thus get

\[
R_1 + r = \left\{ (N_2 + N_3) - (N_1 + N_4) \right\} / 2 = 10.38199 \text{ box ohms.}
= 10.37648 \text{ "legal" ohms.}
= 10.35128 \text{ true ohms.}
\]

Reading of thermometer No. II. = 684.77 millims. = 29\(^\circ-997 \) C.

\( \), bridge-wire = 590.1, and null-point = 599.25 (see p. 288).

Therefore

\[
d' = -0.084 \text{ C.}
\]

* Resistance in battery circuit (2 Leclanché's) = 700 ohms when observing \( N_2 \) and \( N_3 \), and 2900 ohms when observing \( N_1 \) and \( N_4 \).
Hence \( \theta_1 = 29^\circ 913 \) and \( R_1 + r = 10 \cdot 3513 \) true ohms.

therefore, when \( \theta_1 = 30^\circ 000 \) \( R_1 + r = 10 \cdot 3515 \) " , "

The values of \( R_1 + r \) at about \( 30^\circ \) were also ascertained on other dates, and were as follows:

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature</th>
<th>( R_1 + r )</th>
<th>( R_1 + r ) at ( 30^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>September 15</td>
<td>30 \cdot 003</td>
<td>10 \cdot 3516</td>
<td>10 \cdot 3516</td>
</tr>
<tr>
<td>October 5</td>
<td>30 \cdot 245</td>
<td>10 \cdot 3522</td>
<td>10 \cdot 3516</td>
</tr>
<tr>
<td>&quot; 10</td>
<td>30 \cdot 044</td>
<td>10 \cdot 3518</td>
<td>10 \cdot 3517</td>
</tr>
<tr>
<td>&quot; 11</td>
<td>29 \cdot 913</td>
<td>10 \cdot 3513</td>
<td>10 \cdot 3515</td>
</tr>
</tbody>
</table>

I think it unnecessary to multiply examples at other temperatures, the above will show the order of accuracy.

From the above values, the value of \( r (= 0034, \text{ see p. 296) must be subtracted in each case to get the value } R_1 \), given in Table VIII., p. 297.

**Description of Plates 4, 5, and 6.**

**PLATE 4.**

The lower figure is a vertical section of the steel chamber and tank. The spaces filled with mercury are printed in black. The tube at D communicated with the regulating apparatus.

The upper figure is a plan of the lid.

**PLATE 5.**

Fig. 1 is a vertical section of the calorimeter. When gas was driven through the apparatus it entered at \( f \), passed into the bottom of the silver flask \( F \) at \( G \) and left it near the roof at \( d \). It descended to the bottom of the 18 ft. silver coil (sections of which are shown by the small circles at \( C_2 \) ), then ascended a gentle slope and finally left the calorimeter by the tube \( c \). Although in different planes from the section, the position of the platinum thermometer is indicated as well as \( S \), the bottom of the stirrer. A "dropper" is shown in position in the tube \( h \).

Fig. 2 is a horizontal section across the calorimeter at \( AB \) in fig. 1.

Fig. 3 is a plan of the lid.

The stirring shaft passed through \( S \), the platinum thermometer down \( T \), and the tube \( h' \) established communication with the flask \( F \) (fig. 1). The ends of the silver spiral are shown at \( c \) and \( f \).
HEAT OF EVAPORATION OF WATER.

Fig. 4 shows the method of insulating the leads where they passed through the lid of the calorimeter at l and l' (fig. 3), and also the insulation of the four leads where they passed through the steel lid (see small sketch, Plate 6, fig. 3).

PLATE 6.

Fig. 1 is diagrammatic only, for the various tubes, &c., repeatedly crossed each other. The gas on entering passed through H₂SO₄ at S, then through P₂O₅ at P, afterwards through the 30 ft. coil indicated at C, and thus attained to the temperature of the tank water. M₁ is an open scale manometer to show the pressure of the gas when entering the flask F. Leaving this flask near the top, the vapour traversed the coil C₂ and thus attained the temperature of the calorimeter; it then passed through the four-way tap T₄ and on emerging from the tank passed over a row of small gas jets, shown at G. The tubes between T₄ and B could be swept by dry air, by use of the taps T₂ and T₃. All the apparatus within the dotted lines was immersed in the tank water.

Fig. 2 shows the arrangements of the differential thermometers and the bridge. The coil of AB is in series with the compensators of CD and vice versa.

Fig. 3 shows the electrical connections with the calorimeter coil.

A coil in the tank at F was of the same resistance and wire as the calorimeter coil. By means of the key K₁ the current could be switched on to either coil. K₁ was also connected with the chronograph in such a manner that all its movements were recorded.

By means of the Rheochord the external resistance of the storage circuit (leads 2 and 4) could be so adjusted that the D.P. at the points M and N was always that of the Clark cells. Wires numbered 1 and 3 are in the Clark cell circuit.
Calorimeter. 3/4 nat size.
X. Contributions to the Mathematical Theory of Evolution.—II. Skew Variation in Homogeneous Material.

By Karl Pearson, University College, London.

Communicated by Professor Henriot, F.R.S.

Received December 19, 1894,—Read January 24, 1895.

Plates 7–16.

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Section 6.—Illustrations in cases of barometric heights and crab measurements

Section 7.—Fundamental geometrical relation between symmetrical binomial and normal frequency curve

Section 8.—Extension of this relation to the deduction of a skew frequency curve from the asymmetrical binomial

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Section 11.—The hypergeometrical series as replacing the point-binomial. Curves related to the hypergeometrical series in the same manner as the normal curve to the symmetrical point-binomial

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Part I.—Theoretical.

Asymmetrical Frequency Curves.

(1.) An asymmetrical frequency curve may arise from two quite distinct classes of causes. In the first place the material measured may be heterogeneous and may consist of a mixture of two or more homogeneous materials. Such frequency curves, for example, arise when we have a mixed population of two different races, a homogeneous population with a sprinkling of diseased or deformed members, a curve for the frequency of maternity covering more than one class of the population, or in economics a frequency of interest curve for securities of different types of stability—railways and government stocks mixed with mining and financial companies. The treatment of this class of frequency curves requires us to break up the original curve into component parts, or simple frequency curves. This branch of the subject (for the special case of the compound being the sum of two normal curves) has been treated in a paper presented to the Royal Society by the author, on October 18, 1893.

The second class of frequency curves arises in the case of homogeneous material when the tendency to deviation on one side of the mean is unequal to the tendency to deviation on the other side. Such curves arise in many physical, economic and biological investigations, for example, in frequency curves for the height of the barometer, in those for prices and for rates of interest of securities of the same class, in mortality curves, especially the percentage of deaths to cases in all kinds of
fevers, in income tax and house duty returns, and in various types of anthropological measurements. It is this class of curves, which are dealt with in the present paper. The general type of this class of frequency curve will be found to vary (see Plate 7, fig. 1) through all phases from the form close to the negative exponential curve:

\[ y = Ce^{-px}, \]

to a form close to the normal frequency curve

\[ y = Ce^{-p^x}, \]

where C and p are constants.

Hence any theory which is to cover the whole series of these curves must give a curve capable of varying from one to another of these types, \textit{i.e.}, from a type in which the maximum* practically coincides with the extreme ordinate, to a type in which it coincides with the central ordinate as in the normal frequency curve.

It is well known that the points given by the point-binomial \((\frac{1}{2} + \frac{1}{2})^n\) coincide very closely with the contour of a normal frequency curve when \(n\) is only moderately large. For example, the 21 points of \((\frac{1}{2} + \frac{1}{2})^{20}\) lie most closely on a normal frequency curve, and the author has devised a probability machine, which by continually bisecting streams of sand or rape seed for 20 successive falls gives a good normal frequency curve by the heights of the resulting 21 columns. Set to any other ratio \(p:q\) of division other than bisection, the machine gives the binomial \((p + q)^{20}\), or indeed any less power and thus a wide range of asymmetrical point-binomials. Plate 7, fig. 2, represents, diagrammatically, a 14-power binomial machine.

Just as the normal frequency curve may be obtained by running a continuous curve through the point-binomial \((\frac{1}{2} + \frac{1}{2})^n\) when \(n\) is fairly large, so a more general form of the probability curve may be obtained by running a continuous curve through the general binomial \((p + q)^n\). As the great and only true test of the normal curve is: Does it really fit observations and measurements of a symmetrical kind? so the best argument for the generalised probability curve deduced in this paper is that it does fit, and fit surprisingly accurately observations of an asymmetrical character. Indeed, there are very few results which have been represented by the normal curve which do not better fit the generalised probability curve,—a slight degree of asymmetry being probably characteristic of nearly all groups of measurements. Before deducing the generalised probability curve, it may be well to show how any asymmetrical curve may be fitted with its closest point-binomial. This will be the topic of the following five articles.

(2.) Consider a series of rectangles on equal base \(c\) and whose heights are respectively the successive terms of the binomial \((p + q)^n \times a/c\), where \(p + q = 1\). Here \(a\) is clearly the area of the entire system. Choose as origin a point \(O\) distant \(\frac{1}{2}c\) from the

* I have found it convenient to use the term \textit{mode} for the abscissa corresponding to the ordinate of maximum frequency. Thus the "mean," the "mode," and the "median" have all distinct characters important to the statistician.
boundary of the first rectangle, on the line of common bases, and let \( y_r \) be the height of the \( r \)th rectangle, or

\[
y_r = \frac{a}{c} \frac{n(n - 1) \ldots (n - r + 2)}{(r - 1)} p^{n-r+1} q^{r-1},
\]

while

\[
y_1 = \alpha q^n/c.
\]

Let us find the values of

\[
\Sigma \{y_c \times (rc)^r\},
\]

where \( s \) is any integer, for values of \( s \) from 0 to 4.

It is easy to see that

\[
\Sigma \{y_c \times (rc)^r\} = a \alpha^s \left( \frac{d}{dq} \left( q \frac{d}{dq} \left( q \frac{d}{dq} \ldots q (p + q)^n \right) \right) \right),
\]

where the operation \( d/dq \) is repeated \( s \) times.

The operations indicated can easily be performed by putting \( q = e^r \) when

\[
\Sigma \{y_c \times (rc)^r\} = \alpha \alpha^s \left( \frac{d}{dr} \right)^s \{e^r (p + e^r)^n\},
\]

and the successive values can be found by Leibnitz's theorem. After differentiation we may put \( p + q \) or \( p + e^r = 1 \). There results:

\[
\begin{align*}
\Sigma (y_c) &= \alpha \\
\Sigma (y_c \times rc) &= \alpha c \{1 + nq\} \\
\Sigma (y_c \times (rc)^2) &= \alpha c^2 \{1 + 3nq + n(n - 1) q^2\} \\
\Sigma (y_c \times (rc)^3) &= \alpha c^3 \{1 + 7nq + 6n(n - 1) q^2 + n(n - 1)(n - 2) q^3\} \\
\Sigma (y_c \times (rc)^4) &= \alpha c^4 \{1 + 15nq + 25n(n - 1) q^2 + 10n(n - 1)(n - 2) q^3 \\
&\quad+ n(n - 1)(n - 2)(n - 3) q^4\}.
\end{align*}
\]

Let NG be the vertical through the centroid of the system of rectangles, then clearly

\[
ON = \Sigma (y_c \times rc) / \alpha = c \{1 + nq\}.
\]
We shall now proceed to find the first four moments of the system of rectangles round GN. *If the inertia of each rectangle might be considered as concentrated along its mid vertical,* we should have for the $s^{th}$ moment round NG, writing $d = c (1 + nq)$,

$$
\alpha_{s} = \sum \{ y, c \times (rc - d)^{s} \}.
$$

The resulting values are

$$
\mu_{2} = npqc^{2},
\mu_{3} = npq (p - q) c^{3},
\mu_{4} = npq \{ 1 + 3 (n - 2) pq \} c^{4},
$$

whence, remembering that $p + q = 1$, we find that $p$ and $q$ are roots of

$$
z^{2} - z + \frac{(3\mu_{2}^{2} - \mu_{4}) \mu_{2} + \mu_{3}^{2}}{4 (3\mu_{2}^{2} - \mu_{4}) \mu_{2} + 6\mu_{3}^{2}} = 0,
$$

$$
n = \frac{2\mu_{3}^{5}}{(3\mu_{2}^{2} - \mu_{4}) \mu_{2} + \mu_{3}^{2}} \tag{1}
$$

$$
c = \sqrt{\frac{2 (3\mu_{2}^{2} - \mu_{4}) \mu_{2} + 3\mu_{3}^{2}}{\mu_{2}}}.
$$

Thus, when $\mu_{2}$, $\mu_{3}$, and $\mu_{4}$ have been calculated for the frequency curve, the elements of the point-binomial are known. These results were given by me in a letter to ‘Nature,’ October 26, 1893.

They give quite a fair solution so long as $n$ is large and $c$ small, i.e., so long as the asymmetry and the "excess" (*Phil. Trans.,* vol. 185, A, p. 93), measured respectively by $\mu_{3}$ and $\mu_{4} - 3\mu_{2}^{2}$ (which vanish for the normal curve) are not considerable.*

In many cases, however, they are considerable, and the following solution is perfectly general.

* If $y_{0}$ denote the largest term in $(p + q)^{n}$ and $y_{1}$ the $t$th term beyond it, then an application of Stirling’s theorem—if $n$ be large—shows that

$$
y_{t}/y_{0} = (1 - \frac{t}{pn})^{p} (1 + \frac{t}{q} - n - 1)^{x}.
$$

Take

$$
\log u = (t - pn - \frac{1}{2}) \log \left( \frac{t}{pn} \right),
$$

$$
\log v = (n - qn - \frac{1}{2}) \log \left( 1 + \frac{t}{q} \right)
$$

and expand the right hand side in powers of $t$, we find

$$
\log uv = t \left( 1 + \frac{1}{2pn} \right) - \frac{t^{2}}{2pn} \left( 1 - \frac{1}{2pn} \right) - \frac{t^{3}}{6p^{2}n^{2}} \left( 1 - \frac{1}{pn} \right) - \frac{t^{4}}{12p^{3}n^{3}} \left( 1 - \frac{3}{2pn} \right) - \text{etc.}
$$

Hence, remembering that $p + q = 1$, we have

$$
\log uw = -\frac{t (p - q)}{2pq} - \frac{t^{2}}{2npq} \left( 1 - \frac{1}{2npq} \right) + \frac{t^{3}}{6p^{2}q^{2}n^{2}} \left( 1 - \frac{1}{npq} \right) - \frac{t^{4}}{12p^{3}q^{3}n^{3}} \left( 1 - 3pq - \frac{3 (1 - 4pq + 2p^{2}q^{2})}{2npq} \right) - \text{etc.}
$$

Now, making use of the values given in § 2 for $\mu_{2}$, $\mu_{3}$, and $\mu_{4}$, and writing $t \times c = x$, and $y_{t} = y$, we find

$$
2 \times 2
$$
(3.) To find the $n$th moment of a trapezium $ABCD$ about a line parallel to its parallel sides, $y_1$ and $y_2$ being the lengths of the parallel sides, $x_1$, $x_2$, their distances from the moment-axis, and $x_2 - x_1 = c$.

Let $M_n$ be the $n$th moment. Then

$$M_n = \int_{x_1}^{x_2} y x^n \, dx$$

$$= \frac{y_2 - y_1}{x_2 - x_1} \left( \frac{x_2^{n+2} - x_1^{n+2}}{n+2} \right) + \frac{y_1 x_2 - y_2 x_1}{x_2 - x_1} \left( \frac{x_2^{n+1} - x_1^{n+1}}{n+1} \right)$$

$$= y_2 \left( \frac{x_2^n c}{2} - \frac{n}{3} x_2^{n-1} c^2 \right) + \frac{n(n-1)}{4} \left( x_2^{n-2} c^3 - \frac{n(n-1)(n-2)}{5} x_2^{n-3} c^4 \right) + \ldots$$

$$- y_1 \left( \frac{x_1^n c}{2} - \frac{n}{3} x_1^{n-1} c^2 + \frac{n(n-1)}{4} x_1^{n-2} c^3 - \frac{n(n-1)(n-2)}{5} x_1^{n-3} c^4 + \ldots \right).$$

(4.) Now consider a curve of observations made up of a series of trapezia on equal bases, as in the accompanying figure:

$$y = e^{\frac{-x^2}{2\mu_2}} \times e^{\frac{\mu_2}{3\mu_4}} \times e^{\frac{\mu_4}{6\mu_6}} \times e^{\frac{\mu_6}{12\mu_8}} \times e^{\frac{\mu_8}{20\mu_{10}}} \times \text{etc.}$$

where $\beta_1 = \mu_2/\mu_4$ and $\beta_3 = \mu_4/\mu_6$.

This appears to be the more general form of a result given by Professor Edgeworth, "Roy. Soc. Proc.," vol. 56, p. 271.

For the normal curve $\mu_2 = 0$, $\mu_4 = 3\mu_2^2$; hence, if $p$ does not differ much from $q$, $\beta_1$ and $\beta_3$ will be small, and we may neglect their products with $x/\sqrt{\mu_2}$. Thus approximately

$$y = e^{\frac{-x^2}{2\mu_2}} e^{\frac{\mu_2}{3\mu_4}} \left( x - \frac{x^3}{6\mu_4} \right).$$

This agrees with Professor Edgeworth's special case if we expand the second exponential. His "negative frequency" is accounted for by the fact that he has only taken the first terms of a long series, i.e.,

$$y = e^{\frac{-x^2}{2\mu_2}} \left\{ 1 - \frac{\mu_2}{2\mu_4} \left( x - \frac{x^3}{3\mu_4} \right) \right\}.$$

I have not considered this form of the skew-curve at length, because it is only a first approximation to the more general forms considered in this paper, and further, because it is only applicable in practice within extremely narrow limits.
Here \( y_1, y_2, y_3, \ldots y_r \) are the frequencies of deviations falling within the ranges \( x_1 \pm \frac{1}{2}c, x_2 \pm \frac{1}{2}c, x_3 \pm \frac{1}{2}c \ldots x_r \pm \frac{1}{2}c \ldots \), and the tops of the ordinates are joined to form a frequency-curve in the usual manner.

Let \( M'_n \) be the \( n \)th moment of the system of trapezia about the line \( Oy \), then

\[
M'_n = S \left\{ 2y_r \left( \frac{x_r c}{2} + \frac{n(n-1)}{12} x_r^3 + \frac{n(n-1)(n-2)(n-3)}{360} x_r^5 + \ldots \right) \right\}
\]

In particular, if we take \( Oy \) in the position \( O'y' \) at distance \( c \) from \( y_1 \), we have \( x_r = re \), and accordingly,

\[
M'_n = c^{n+1} \left( N'_n + \frac{n(n-1)}{12} N'_{n-2} + \frac{n(n-1)(n-2)(n-3)}{360} N'_{n-4} \right. \\
+ \frac{n(n-1)(n-2)(n-3)(n-4)(n-5)}{20160} N'_{n-6} + \ldots \right)
\]

where \( N'_n = S (y_r x_r^2) \).

In particular,

\[
M'_0 = c N'_0, \\
M'_1 = c^3 N'_1, \\
M'_2 = c^3 (N'_2 + \frac{1}{6} N'_0), \\
M'_3 = c^4 (N'_3 + \frac{1}{2} N'_1), \\
M'_4 = c^5 (N'_4 + N'_3 + \frac{1}{5} N'_0), \\
M'_5 = c^6 (N'_5 + \frac{5}{3} N'_3 + \frac{1}{3} N'_1).
\]

When we put \( M'_n/M'_0 = \mu'_n \), and \( N'_n/N'_0 = \nu'_n \), these reduce to

\[
\mu'_1 = c \nu'_1, \\
\mu'_2 = c^3 (\nu'_2 + \frac{1}{3} \nu'_0), \\
\mu'_3 = c^3 (\nu'_3 + \frac{1}{2} \nu'_1), \\
\mu'_4 = c^4 (\nu'_4 + \nu'_3 + \frac{1}{5} \nu'_0), \\
\mu'_5 = c^5 (\nu'_5 + \frac{5}{3} \nu'_3 + \frac{1}{3} \nu'_1).
\]

Now let \( \mu_n \) be the value of the \( n \)th moment of the trapezia system about its vertical through its centroid divided by its area.
We have:

\[ \mu_n = \mu' - np_1 \mu'_2 + n(n - 1) \mu'_3 + \frac{n(n - 1)(n - 2)}{3} \mu'_4 + \text{etc.} \]

Thus we find:

\[ \mu_1 = 0, \]
\[ \mu_2 = c^2 (p_2 - \frac{1}{3} + \frac{1}{6}), \]
\[ \mu_3 = c^3 (3p_1 p_2 + 2p_1^3), \]
\[ \mu_4 = c_4 (p_4 - 4p_1 p_3 + 6p_1^2 p_2 - 3p_1^4 + \{p_1^2 - \frac{1}{3} + \frac{1}{6} \}), \]
\[ \mu_5 = c^5 (p_5 - 5p_1 p_4 + 10p_1^2 p_3 - 10p_1^3 p_2 + 4p_1^4 + \{\frac{5}{3} p_1^3 - 5p_1 p_2 + \frac{10}{3} p_1^3 \}). \]

Comparing these results with those given in the 'Phil. Trans.' vol. 185, p. 79, Eq. (4), we see that treating the curve as built-up of trapezia instead of loaded ordinates introduces the parts into the values of the \( \mu \)'s enclosed in curled brackets. These additions are small, but in many cases quite sensible. Since the series of trapezia gives in general a closer approach than the series of loaded ordinates to the frequency curve, and, further, since the calculation of these additional terms is not very laborious, it will be better for the future to calculate the moments of any frequency curve from the above modified formulae.

(5.) Returning now to the point-binomial, we have:

\[ p'_{1} = 1 + nq, \]
\[ p'_{2} = 1 + 3nq + n(n - 1)q^2, \]
\[ p'_{3} = 1 + 7nq + 6n(n - 1)q^2 + n(n - 1)(n - 2)q^3, \]
\[ p'_{4} = 1 + 15nq + 25n(n - 1)q^2 + 10n(n - 1)(n - 2)q^3 \]
\[ + n(n - 1)(n - 2)(n - 3)q^4. \]

Thus:

\[ \mu_2 = c^2 (npq + \frac{1}{6}), \]
\[ \mu_3 = -c^3 npq (q - p), \]
\[ \mu_4 = c^4 (\frac{1}{6} + npq (2 + 3(n - 2)pq)). \]

If, instead of taking trapezia, we had taken a series of rectangles, but not, as in §2, concentrated their areas along their axes, we should have found the following system:

\[ \mu_2 = c^2 (npq + \frac{1}{12}), \]
\[ \mu_3 = -c^3 npq (q - p), \]
\[ \mu_4 = c^4 (\frac{1}{8} + npq (\frac{3}{2} + 3(n - 2)pq)). \]
Hence if we write:
\[
\begin{align*}
\mu_2 &= c^2 (npq + \epsilon_1), \\
\mu_3 &= -c^3 npq (q - p), \\
\mu_4 &= c^4 (\epsilon_2 + npq (\epsilon_3 + 3(n-2)pq)),
\end{align*}
\]
we have:

For trapezia:  \( \epsilon_1 = \frac{1}{6}, \quad \epsilon_2 = \frac{1}{3}, \quad \epsilon_3 = 2, \)

For rectangles:  \( \epsilon_1 = \frac{1}{2}, \quad \epsilon_2 = \frac{1}{3}, \quad \epsilon_3 = 1.5, \)

For loaded ordinates:  \( \epsilon_1 = 0, \quad \epsilon_2 = 0, \quad \epsilon_3 = 1, \)

and the above general system may be applied to all cases.

Writing
\[
z = npq, \quad \beta_1 = \frac{\mu_2}{\mu_3^2}, \quad \text{and} \quad \beta_2 = \frac{\mu_3}{\mu_4^2},
\]
we have by elimination the cubic for \( z \):
\[
z^3 (6 + 3\beta_1 - 2\beta_2) + z^2 (2\epsilon_3 - 3 + 9\beta_1\epsilon_1 - 4\beta_2\epsilon_1)
+ z (2\epsilon_2 + 9\beta_1\epsilon_1^2 - 2\beta_2\epsilon_1^3) + 3\beta_1\epsilon_1^3 = 0.
\]

The remaining constants of the binomial are:
\[
n = \frac{4z}{1 - \beta_1^2 (1 + \epsilon_1/z)^3},
\]
\[
pq = \frac{1}{4} (1 - \beta_1 z (1 + \epsilon_1/z)^3),
\]
and
\[
c = \sqrt{\frac{\mu_3}{z + \epsilon_1}}.\]

(6.) Let us illustrate these results by a numerical example. Plate 8 gives Dr. Venn's curve for 4857 barometric heights. Along the horizontal, 1 cm. equals 1" of height of barometer, and the scale of frequency is 1 sq. cm. = 28.304 observations. The centroid vertical and the second, third, and fourth moments about it were found for me\( \dagger \) by the graphical process described, 'Phil. Trans.,' vol. 183, p. 79. We have the following results:—

\* This result seems of considerable importance, and I do not believe it has yet been noticed. It gives the mean square error for any binomial distribution, and we see that for most practical purposes it is identical with the value \( \sqrt{npq} \) hitherto deduced as an approximate result, by assuming the binomial to be approximately a normal curve.

\( \dagger \) If we take \( z + \epsilon_1 = \chi \) the fundamental cubic reduces to
\[
(6 + 3\beta_1 - 2\beta_2) \chi^3 - (2 - \frac{3}{2} \beta_2) \chi^2 + \epsilon_1 \chi - \frac{\epsilon_1^3}{4} = 0,
\]
a form in which the coefficients are easily calculated and the nature of the roots discriminated.

\( \dagger \) By Mr. G. U. Yule, who has given me very great assistance in the laborious calculations required in the reduction of frequency curves. We have used, with much economy of time, the "Brunsviga" calculator.
$\alpha = 171.6$, \\
$\mu_2 = 10.14$, \\
$\mu_3 = 15.95$, \\
$\mu_4 = 326.34$, \\
all in centimetre units.

These give

$\beta_1 = 24401$, $\beta_2 = 3.1739$.

Hence for trapezia,

$\cdot3842z^3 - \cdot749917z^2 + \cdot018008z + \cdot003389 = 0$,

and for rectangles,

$\cdot3842z^3 - \cdot87496z^2 + \cdot003832z + \cdot000424 = 0$.

These give the following solutions:

<table>
<thead>
<tr>
<th></th>
<th>Trapezia.</th>
<th>Rectangles.</th>
<th>Lines.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z$</td>
<td>1.92516</td>
<td>2.28034</td>
<td>2.6028</td>
</tr>
<tr>
<td>$u$</td>
<td>10.379</td>
<td>23.983</td>
<td>28.5203</td>
</tr>
<tr>
<td>$p$</td>
<td>8.881</td>
<td>8.936</td>
<td>-8.9985</td>
</tr>
<tr>
<td>$q$</td>
<td>11.19</td>
<td>10.64</td>
<td>-1.0015</td>
</tr>
<tr>
<td>$c$</td>
<td>2.2017</td>
<td>2.0712</td>
<td>1.974</td>
</tr>
<tr>
<td>$a/b$</td>
<td>77.94</td>
<td>82.85</td>
<td>86.93</td>
</tr>
<tr>
<td>$d$</td>
<td>6.976</td>
<td>7.3562</td>
<td>7.614</td>
</tr>
</tbody>
</table>

Here $d = c(1 + uq)$ gives the distance of the start of the point-binomial from the centroid vertical. The three point-binomials are therefore

$77.94(8.881 + 11.19)^{1.0579}$,

$82.85(8.936 + 10.64)^{1.23983}$,

$86.93(8.9985 + 1.0015)^{1.23983}$,

respectively.

These three point-binomials are represented in Plate 8, fig. 3. It will be noticed that they all lie very close to the barometric curve; they would be still closer if that curve were a real curve and not a polygonal line. The total areas between binomial-polygons and observation curves, treating all parts as positive, are for the three cases, 10.3, 10.5, 11.0 sq. centims. respectively, or taking the base range to be 23 centims., we have mean deviations from the observation curve of 448, 457, 478 in the three cases respectively. Thus the method of trapezia gives slightly the best result; the method of concentrating along ordinates wins the worst result. The total area of the curve being 171.6, we have from another standpoint, mean percentage errors* in the ordinates of about 6.03, 6.06, and 6.3, respectively. The generalised probability curve, if fitted to the same observations, gives an areal deviation of 7 sq. centims., or a percentage error of about 4. Thus it is very nearly one-third as close again as the point-binomials.

* The "percentage error" in ordinate is, of course, only a rough test of the goodness of fit, but I have used it in default of a better.
As typical samples of mean percentage errors considered by various statisticians to give good results, I may note the following, the frequency being about 1,000 or upwards:—Airy, 9; Merri man, 13·5; Galton (Anthropometric), 7 to 15; Weldon (Crabs), 6·7, (Shrimps), 8·8; Stieda (Skulls), 7·6; Porter (School Girls), 7·7; Per ozzo (Recruits), 6·8; Bradley’s observations, 5·85; Pearson (Lottery), 6·7, (Tossing), 6·6.

It is therefore clear that our point-binomials and generalized curve may be considered to give good results.* It will be noticed, however, that a little difference in the method of calculating the point-binomials leads, without much alteration of the percentage error, to a considerable change in their centroid-positions and the magnitude of their constants.† Generally speaking we may conclude that in round numbers the barometric frequency corresponds to the binomial $(9 + 1)^3$, or to the distribution of zeros when 20 ten-sided teetotums, marked 0, 1 . . . 9, are spun together. There is an apparent upper limit to the height of the barometer, and its deviation below the mean can be much greater than its deviation above. At the same time within the narrower range round the mean, the frequency of a high barometer is greater than the frequency of a low barometer; the odds against a “contributory cause” tending to a low barometer being about 9 to 1. I propose to investigate a wider series of barometric observations, in order to test how far the conclusions which may be drawn from Dr. Venn’s statistics are general.‡

A rather interesting point may be considered at this stage. Is it always possible to fit a point-binomial to a series of observations with a chance frequency? Can we better the normal curve by a point-binomial? The answer is Yes, if the fundamental cubic in $\chi$ (second footnote, p. 351), has a real positive root. Now for the normal curve $2 (3\mu_2^2 - \mu_1) \mu_2 + 3\mu_3^2$, or $6 + 3\beta_1 - 2\beta_2$ is zero. For the loaded ordinates $c$ will only be real if this expression be positive. It may, however, take small negative values for the trapezia, in which case $\chi$ itself will be small and only within narrow limits give suitable values for $n$.

Hence, for real values of $n, p$ and $q$, it is impossible to fit a point-binomial to a series of observations for which $6 + 3\beta_1 - 2\beta_2$ has a large negative value. The normal curve, for which $\mu_1 = 3\mu_2$, is nearer to any such observations than a point-binomial.

For example, by aid of the modified expressions given in this paper, p. 350, we have

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* As another manner of testing, compare the ten-points of the point-binomial for lines with observations:

<table>
<thead>
<tr>
<th>Theory</th>
<th>5·6</th>
<th>15·9</th>
<th>21·8</th>
<th>19</th>
<th>11·9</th>
<th>5·7</th>
<th>21·1</th>
<th>7·2</th>
<th>0·3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation</td>
<td>5·7</td>
<td>15·8</td>
<td>22·1</td>
<td>18·8</td>
<td>12</td>
<td>5·8</td>
<td>2·3</td>
<td>1·1</td>
<td>2·0</td>
</tr>
</tbody>
</table>

† A curve drawn through the 30 points of the three point-binomials would be very close to the observations. As a matter of fact, the skew probability curve passes very near to all 30 points.

‡ [Miss A. Lee has since calculated the constants of three years of Eastbourne barometric observations for me. While $a$ and $c$ differ widely from the Cambridge values, she finds $p = 89375$, $q = 10625$, a striking and suggestive agreement.]
for the data given for Professor Weldon's Crab Measurements, No. 4, 'Phil. Trans.,' A, vol. 185, p. 96.

$$\mu_2 = 7.6759, \quad \mu_3 = 3.4751, \quad \mu_4 = 184.3039.$$  

Hence,

$$\beta_1 = \frac{\mu_3^3}{\mu_2^3} = 0.0267022,$$

$$\beta_2 = \frac{\mu_4}{\mu_2^2} = 3.12807.$$  

Thus $6 + 3\beta_1 - 2\beta_2$ is positive, and accordingly no rational point-binomial is likely to fit as well as the normal curve. As a matter of fact the fundamental cubic is now

$$17603z^3 + 1.045327z^2 + 0.03773z - 0.003709 = 0.$$  

The two negative roots of this equation give imaginary value for $p$ and $q$. The small positive root gives $p$ greater than unity and $q$ negative, $n$ is also negative. Although I can give no interpretation to these results, it seemed well to complete in the latter case the solution and test how near the resulting point-binomial fitted the curves. I found

$$z = 0.00866, \quad p = 1.19268, \quad q = -1.19268.$$

$$n = -0.037685, \quad c = 6.61662, \quad d = 6.6645.$$  

These give for the binomial

$$150.0983 \left(1.19268 - 1.19268\right)^{-0.037685},$$  

or,

$$151.89 \left(1 - 1.161552\right)^{-0.037685},$$  

or,

$$151.89 + 92532 + 0.7756 + \&c.$$  

Thus the sensible part of the binomial to the scale of our figure is a triangle. I have drawn this binomial, see Plate 8, fig. 4. The reader will mark a fit very close on the whole to the observations. We have the following percentage mean errors of the ordinates:—

<table>
<thead>
<tr>
<th>Curve</th>
<th>Mean Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal curve</td>
<td>6.7</td>
</tr>
<tr>
<td>Skew probability curve</td>
<td>4.4</td>
</tr>
<tr>
<td>Binomial</td>
<td>10.5</td>
</tr>
</tbody>
</table>

We may conclude, therefore, that even if our binomial constants have unintelligible values, yet our method will give, in many cases, a closely-fitting polygonal figure. This remark should be read in connection with Professor Edgeworth's somewhat divergent views* on fitting chance distributions with curves other than the normal error curve. It is possible in almost every case to find simple combinations of lines,

---

* See 'Phil. Mag.,' vol. 334, p. 24, et seq., 1887.
circles, or parabolas of various degrees which give results extremely close to any given set of observations.

For example, taking the range of frequency to be sensibly \( \pi \) times the standard deviation, we have the following close expression for the error function by harmonic analysis

\[
y = y_0 \left\{ 0.399 \cos \frac{x}{\sigma} + 1.09 \cos \frac{2x}{\sigma} + 0.009 \cos \frac{3x}{\sigma} \right\}.
\]

Here \( y_0 \) is the maximum ordinate, \( x \) any deviation, and \( \sigma \) the standard deviation. A couple of wave curves* will thus very frequently give us a close approximation to a set of statistical measurements, quite as close as statistical practice shows the error curve to be.

The above expression further allows the normal curve to be constructed by aid of scale and compasses—geometrically, or its ordinates calculated from a table of cosines.

Another example of the fitting of a point-binomial will be found in Part 2, \S\ 34, Pauper Percentages.

(7.) Consider the point-binomial \( e \times (\frac{1}{2} + \frac{1}{2})^r \), where \( e \) is any constant, and suppose a polygon formed by plotting up the terms of the binomial at distance \( c \) from each other.

Then, corresponding to \( x_r = rc \), we have

\[
y_r = e \frac{n(n-1)(n-2) \ldots (n-r+2)}{(r-1)!} \left( \frac{1}{2} \right)^r
\]

and

\[
\frac{y_{r+1} - y_r}{\frac{1}{2}(y_{r+1} + y_r)} \times e = \frac{e(n+2) - (x_r + x_{r+1})}{\frac{1}{2}(n+1) c^2} = \frac{(x_r' + x_{r+1}')}{\frac{1}{2}(n+1) c^2},
\]

if \( x_r' = x_r - \frac{1}{2}c(n + 2) \).

Now \( (y_{r+1} - y_r)/e \) is the slope of the polygon corresponding to the mean ordinate \( \frac{1}{2}(y_{r+1} + y_r) \), or, writing\( \sigma^2 = \frac{1}{2} \times \frac{1}{2} (n + 1) c^2 \),

\[
\frac{\text{slope of polygon}}{\text{mean ordinate}} = -\frac{2 \times \text{mean abscissa}}{2\sigma^2}.
\]

* It is often sufficient to take

\[
y = y_0 \left( \frac{1}{2} + \frac{1}{2} \cos \frac{x}{\sigma} + \frac{1}{2} \cos \frac{2x}{\sigma} \right).
\]

† The divergence of this value of \( \sigma^2 \) from the ordinary value \( \frac{1}{2} \times \frac{1}{2} \times n \) is to be noted. The two agree sensibly if \( n \) be great. [Drawing on a large scale, however, the point-binomial \((\frac{1}{2} + \frac{1}{2})^{10}\) and the two normal curves with standard deviations of 1.5311 and 1.6533, I find that the latter has a mean percentage error of only 1.76 as compared with 5.1 of the former. Thus it would appear that the normal curve corresponding to \( \sqrt{(n + 1) pq} \) fits the point-binomial closer than one with the standard deviation \( \sqrt{npq} \) usually adopted.]
Now compare this property of the polygon with that of the curve:

\[ y = y_0 e^{-\frac{x^2}{2\sigma^2}}. \]

We have by differentiation:

\[
\frac{\text{slope of curve}}{\text{ordinate}} = -\frac{2 \text{abscissa}}{2\sigma^2}.
\]

Hence: this binomial polygon and the normal curve of frequency have a very close relation to each other, of a geometrical nature, which is quite independent of the magnitude of \( n \). In short their slopes are given by an identical relation. By a proper choice of \( \sigma \) and \( y_0 \), we can get the normal curve to fit closely the point-binomial, owing to this slope property, without any assumption as to the indefinitely great value of \( n \). It is this geometrical property which is largely the justification for the manner in which statisticians apply, and apply with success, the normal curve to cases in which \( n \) is undoubtedly small. No stress seems hitherto to have been laid upon the fact that the normal curve of errors besides being the limit of a symmetrical point-binomial has also this intimate geometrical relationship with it.*

(8.) Now let us deal with the skew point-binomial in precisely the same manner as we have dealt with the symmetrical binomial. Taking its form to be \( c (p + q)^n \), we have, if \( x_r = r \times c \) and \( \lambda = q/p \):

\[
\frac{y_r + 1 - y_r}{\frac{1}{2} (y_r + 1) c} = \frac{2 (n - r + 1) \lambda r - 1}{c (n - r + 1) \lambda r + 1} = \frac{2 (\lambda (n + 1) - \lambda (\lambda + 1))}{c (\lambda (n + 1) + r (1 - \lambda))}.
\]

Let us write \( \Delta y = y_{r+1} - y_r \), \( \Delta x = c \).

\[
\Delta x r + 1 = \frac{1}{2} (y_{r+1} + y_r), \quad X_{r+1} = \frac{1}{2} (x_{r+1} + x_r).
\]

Then \( X_{r+1} / \sigma = r + \frac{1}{2} \), and:

* The following table shows the closeness of frequency within a given range as determined by the binomials:

<table>
<thead>
<tr>
<th>Range of deviation.</th>
<th>Frequency per cent. ((1 + 1)^{10})</th>
<th>((1 + 1)^{20})</th>
<th>Normal curve.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>24</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>87</td>
<td>37</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>71</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>15</td>
<td>87</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>21</td>
<td>96</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>33</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Here the distribution of 100 groups each of 100 events is seen to be practically the same whether we take \( n = 10 \) or \( n = \infty \).
\[
\frac{\Delta y}{\Delta x \times y_{r+1}} = \frac{2}{c} \cdot \frac{\lambda (n + 1) - (1 + \lambda) \left( \frac{X_{r+1}}{c} - \frac{1}{2} \right)}{\lambda (n + 1) + (1 - \lambda) \left( \frac{X_{r+1}}{c} - \frac{1}{2} \right)},
\]

or, if \( X_{r+1} = X_{r+1} - c \left( \frac{1}{2} + q (n + 1) \right) \),

\[
= \frac{-X'_{r+1}}{pq (n + 1) c^2 + p - q \frac{c}{2} X'_{r+1}}
\]

\[
= \frac{-\gamma X'_{r+1}}{\alpha + X'_{r+1}},
\]

if \( \gamma = \frac{2}{(p - q)c} \) and \( \alpha = \frac{2pq (n + 1) c}{p - q} \).

The curve which has the same law of slope as this skew binomial is:

\[
y = y_0 (1 + x/\alpha)^{\alpha} e^{-x^2}.
\]

(9.) This curve accordingly stands in the same relationship to the skew binomial as the normal curve to the symmetrical binomial.* There are several points, however, to be considered with regard to it. In the first place it is usually assumed that \( n \) is indefinitely great and \( c \) indefinitely small, and then it is supposed that we may neglect \((p - q) c X'_{r+1}\) as compared with \(pq (n + 1) c^2\), and so we deduce the normal error curve whether \( p \) be equal to \( q \) or not. But I contend that this is unjustifiable except for very small values of \( X'_{r+1} \). When the deviation \( X' \) is considerable and \( c \) vanishingly small, \( X' \) will be an indefinitely great multiple of \( c \); \( c \) must be in fact the unit in which \( X' \) is measured and unless \( p = q \), the ordinary normal curve is only an approximation, even if \( n \) be large, near the maximum frequency. In the next place, when we speak of \( n \) being large, are we quite clear as to what we mean in the case of physical or biological frequency curves? We speak of a multiplicity of small "causes" determining the actual dimensions of an organ, or the size of a physical error, or the height of the barometer. But it is less clear why this multiplicity should be identified with the infinite greatness of \( n \). If we take Dr. Venn's frequency curve for barometric height, we see that the closest point-binomial is by no means consistent with either \( p = q \), or with \( n \) being indefinitely great. Further, many statistical results in games of chance are given with great exactness by the normal curve, although we are then able to show that \( n \) is quite moderate.

Now, it is true that the biological and physical statistics to which we are referring, give essentially continuous curves, but it does not seem to follow of necessity that \( n \) must be infinite; while their frequent skewness sufficiently indicates that the neglect

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* Note again the deviation of the constant \( pq (n + 1) c^2 \) from its usually adopted value \( pqn c^2 \).
of $X'_{r+1}$ as compared with $\alpha$ is unjustifiable. Thus, the maximum of a fever mortality curve cannot be an infinite distance from birth, which limits the curve in one direction, nor an age-at-marriage curve have a maximum frequency infinitely distant from the age of puberty, nor a frequency of interest curve separate its maximum, between 3 or 4 per cent., by an infinite distance from 0 per cent. It is clear, therefore, that if such frequency curves as those referred to are to be treated as chance distributions at all, it would be idle to compare them to the limit of a symmetrical binomial. We are really quite ignorant as to the nature of the contributory "causes" in biological, physical, or economic frequency curves. The continuity of such frequency curves may depend upon other features than the magnitude of $n$. If I toss twenty coins, a discrete series of 0, 1, 2, 3, \ldots 20, heads is the only possible range of results. Each individual coin, here representing a "contributory cause" can only give head or tail, and so many whole coins must give head, so many tail. If I want to make any ratio of head to tail, I have to take an indefinitely great number of coins, for each "contributory cause" must give a unit to the total. But it may possibly be that continuity in biological or physical frequency curves may arise from a limited number of "contributory causes" with a power of fractionizing the result. We cannot conceive on the tossing of 20 coins that 13.5 will give heads and 6.5 will give tails, we are obliged to deal with 200 coins, 133 giving heads and 67 tails. Yet the two things are not identical. The former corresponds to a value intermediate between two ordinates of $(\frac{1}{2} + \frac{1}{2})^{20}$, and the latter to a definite ordinate of $(\frac{1}{2} + \frac{1}{2})^{200}$. So long as we remain in ignorance of the nature and number of "contributory causes" in physics and biology, so long as we do find markedly skew distributions, it seems to me that we must seek more general results than flow from the assumption that $p = q$ and $n = \infty$. The form of curve given in § 8 above is suggested as a possible form for skew frequency curves. Its justification lies essentially, like that of the normal curve, in its capacity to express statistical observations.

(10.) But it must be noted that the generalised probability curve in § 8, although it contains the normal curve as a special case, is not sufficiently general. It is limited in one direction, indefinitely extended in the other. This limitation at one end only, corresponds theoretically to many cases in economics, physics, and biology. But there are a great variety of cases in which there is theoretical limitation at both

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure}
\caption{Diagram of trapezium.}
\end{figure}

ends; that is to say, there is a limited range of possible deviations. For example, let a trapezium, ABCD, of white paper be pasted on a cylinder of black surface with
the axis of symmetry parallel to the axis of the cylinder. Then, if the cylinder be rotated, we shall have a series of grey tints from a darkish e to a lighter f. Now, if we ask several hundred persons to select a tint which would result from mixing the tints at e and f, we shall obtain a continuous frequency curve, falling, however, entirely within the range e to f. Or, again suppose a frequency curve obtained by plotting up the frequency of a given ratio of leg-length to total body-length, or of carapace to body-length. Here the range must lie between 0 and 1. It is not that other values are excessively improbable, they are by the conditions of the problem absolutely impossible. Hence, it is clear that the curves obtained by Professor Weldon and Mr. H. Thompson in the case of shrimps, crabs, and prawns, can only be approximately normal curves, even if it were possible for the ratios to run from 0 to 1. But as a matter of fact, the possible range is very much smaller. We may not be able to assert, à priori, what it is, but for an adult prawn to have a carapace $\frac{2}{3}$ or $\frac{1}{1000}$ of its body-length, or a man a leg $\frac{3}{4}$ or $\frac{7}{10}$ of his body-length, may be regarded as impossibilities; they are abnormalities, which could hardly survive to the adult condition. Precisely the same remarks apply to skull indices, and probably to the relative size of all sorts of organs in the adult condition. We may not know the range, à priori, but we are quite certain that it exists, and it is a quantity to be determined—just as the mean or the standard deviation—from our measurements themselves. We may take it that in most biological measurements of adults there is a range of stability, so to speak, organs not falling within this range are inconsistent with the continued existence of the individual, with the assumption that he has lived to be an adult. Nor is this question of range confined to biological statistics. A barometric frequency curve must show the same peculiarity; there are excessively low and excessively high barometric heights which would be not only inconsistent with the survival of any meteorological observer, but also with the existing features of physical nature on this earth. In vital statistics we find precisely the same thing, a curve of percentages of mothers of different ages for the children born during any year in a country would be definitely limited by the ages of puberty and the climacteric, which cannot be pushed indefinitely towards childhood and senility respectively. Again in disease and mortality curves, while the lower limit of life is clear, it is highly probable that an upper limit exists, if we can only fix it by investigation of our statistics themselves. A man of the present day, as now organised, may be able to live 120 years, perhaps, but we have exceeded his vital possibilities if we take, say, 200 years.

Thus the problem of range seems a very important one, it theoretically excludes the use of the normal curve in many classes of statistics; it is quite true that, for many practical purposes, frequency curves of limited range may be sensibly identical either with unlimited curves, or even with normal curves, but, in other cases, this

* Absolute malformations, congenital, or due to post-natal accident are excluded. Abortions or amputations would be naturally excluded from our measurements.
is not so, and under any circumstances the limited curve may actually give information as to the possible range—the "limits of stability"—which is itself of great value.

We have, then, reached this point: that to deal effectively with statistics we require generalised probability curves which include the factors of skewness and range. The generalised curve we have already reached, possesses skewness, but its range is limited in one direction only.

Accordingly, we require the following types of frequency curves:

Type I.—Limited range in both directions, and skewness.

Type II.—Limited range and symmetry.

Type III.—Limited range in one direction only and skewness.

Type IV.—Unlimited range in both directions and skewness.

Type V.—Unlimited range in both directions and symmetry.

Type V. is the normal curve; Type IV., with slight skewness, has been dealt with by Poisson in the form of an approximative series.* Type III. has been given above, it was first published by me without discussion in 'Roy. Soc. Proc.,' vol. 54, p. 331.

We can now turn to the general problem.

(11.) A very simple example will illustrate how a frequency curve, with limited range and skewness, may be considered to arise. Take $n$ balls in a bag, of which $pn$ are black, and $qn$ are white, and let $r$ balls be drawn and the number of black be recorded. If $r > pn$, the range of black balls will lie between $o$ and $pn$; the resulting frequency polygon will be skew and limited in range. This polygon, which is given by a hypergeometrical series, leads us to generalised probability curves, in the same manner as the symmetrical and skew binomials lead us to special cases of such curves. If we consider our balls to become fine shot, or ultimately sand, and suppose each individual grain to have an equal chance of being drawn, we obtain a continuous curve.† It is not, however, impossible that, could we measure with sufficient accuracy, many physical as well as biological statistics might be found to proceed by units, much as in certain types of economic statistics we are not troubled with fractions of a penny. For this reason we shall keep our results in the most general form, and obtain a curve approximating to the hypergeometrical series referred to without any assumptions as to the relative magnitude of the quantities involved.

We easily obtain for the series giving the chances of $r, r - 1, r - 2 \ldots 0$, black balls being drawn out of a bag containing $pn$, black, and $qn$, white, the expression

---

† $p$ pints of red sand and $q$ pints of white sand are put into a vessel, and $r$ pints are withdrawn. We have if $r > p$, a perfectly continuous frequency curve for red sand withdrawn ranging between $o$ and $p$ pints. We are here supposing no "perfect mixture" of the two kinds of sand, but theoretical equality of chances for each grain.
If \( y_s \) be the \( s \)th ordinate of this polygon, and we suppose these ordinates plotted up at distances \( c \) apart, we have

\[
\frac{y_{s+1}}{y_s} = \frac{r - s + 1}{s} \frac{q_n - s + 1}{q_n - r + s},
\]

\[
x_s = s \times c, \quad x_{s+1} = (s + 1) c,
\]

Thus

\[
\frac{y_{s+1} - y_s}{\frac{1}{2} (y_{s+1} + y_s) \times c} = \frac{2}{c} \left( \frac{r + 1}{1 + q_n} - s \frac{1}{n + 2} \right)
\]

\[
= \frac{(r + 1) (1 + q_n) - \left( \frac{X_{s+1}}{c} \right) - \frac{1}{2} (n + 2)}{(r + 1) (1 + q_n) - \left( \frac{X_{s+1}}{c} \right) - \frac{1}{2} (2 (r + 1) + n (q - p)) + 2 \left( \frac{X_{s+1}}{c} \right)}.
\]

Write

\[
X'_{s+1} = X_{s+1} - c \left( \frac{1}{2} + \frac{(r + 1) (1 + q_n)}{n + 2} \right),
\]

and we find with our previous notation

\[
\frac{\Delta y}{\Delta x} Y_{s+1} = \frac{-X_{s+1}'}{\beta_1 + \beta_2 X_{s+1}' + \beta_3 X_{s+1}''},
\]

where

\[
\beta_1 = \frac{c^2 (r + 1) (n - r + 1) (1 + q_n) (1 + p_n)}{(n + 2)^3},
\]

\[
\beta_2 = \frac{c n (n - 2 r) (p - q)}{2 (n + 2)^3}, \quad \beta_3 = \frac{1}{n + 2}.
\]

Now, if we attempt to find the curve which has the same geometrical relation for the slope as the above hypergeometrical polygon, we see that it will change its type according to the sign of \( \beta_2^3 - 4 \beta_1 \beta_3 \).

After some reductions we have

\[
\sqrt[3]{\beta_2^3 - 4 \beta_1 \beta_3} = \frac{c n}{n + 2} \left( \frac{1}{2} - \sqrt{\left( p + \frac{1}{n} \right) \left( q + \frac{1}{n} \right) - \frac{r}{n}} \right) \left( \frac{1}{2} + \sqrt{\left( p + \frac{1}{n} \right) \left( q + \frac{1}{n} \right) - \frac{r}{n}} \right).
\]
Hence \( \sqrt{\beta_3^2 - 4\beta_2\beta_3} \) will be real or imaginary, according as \( r/n \) lies outside or between the limits

\[
\frac{1}{2} \pm \sqrt{\left\{ \frac{1}{n} \left( p + \frac{1}{n} \right) \left( q + \frac{1}{n} \right) \right\}}.
\]

If \( r/n \) lies outside these limits, then the integral of the right-hand side of equation (e) is purely logarithmic; if it lies between these limits, the integral is in part trigonometrical.

Since \( r \) must be less than \( n \), it follows that the integral must be trigonometrical if these limits are respectively \( = <0 \) and \( = >1 \), i.e., if

\[
(p + 1/n) (q + 1/n) = \text{or} > \frac{1}{4},
\]

or \( p \) must lie between \( \frac{1}{2} \pm \sqrt{\left\{ \frac{1}{n} \left( 1 + \frac{1}{n} \right) \right\}} \).

For example, if \( n = 100 \), then, if \( p \) lies between \( 6005 \) and \( 3995 \), the integral must be trigonometrical. If \( p \) lies outside these limits, say \( = 7 \) for example, then the integral will be logarithmic if \( r/n \) does not lie between \( 04 \) and \( 96 \), i.e., if we draw a small or large proportion of the total contents.

Let us treat the trigonometrical and logarithmic cases separately.

(12.) Case I. \( \beta_3^2 < 4\beta_2\beta_3 \).

The curve having the same geometrical slope relation is

\[
\log y = \text{constant} - \frac{1}{2\beta_3} \log (\beta_1 + \beta_2x + \beta_3x^2)
\]

\[
- \frac{\beta_3}{2\beta_3} \frac{2}{\sqrt{\{4\beta_1\beta_3 - \beta_2^2\}}} \tan^{-1} \frac{2\beta_3x + \beta_2}{\sqrt{4\beta_1\beta_3 - \beta_2^2}}.
\]

Write \( x \) for \( x + \beta_2/2\beta_3 \), changing the origin; further put \( \alpha \) for \( \sqrt{\{4\beta_1\beta_3 - \beta_2^2\}/(2\beta_3)} \), \( m \) for \( 1/(2\beta_3) \), and \( \nu \) for \( \beta_3/\sqrt{4\beta_1\beta_3 - \beta_2^2} \), then we have, \( y_0 \) being a constant of integration,

\[
y = \frac{y_0}{(1 + x^2/\alpha^2)^m} e^{-\nu \tan^{-1}(x/\alpha)}.
\]

This frequency curve is asymmetrical and has an unlimited range on either side of the origin. It corresponds accordingly to the curve required as Type IV.

Here

\[
\alpha = \frac{1}{4} c \sqrt{\{4 (1 + pn) (1 + qn) - (n - 2r)^2\}},
\]

\[
\nu = \frac{n(n - 2r)(p - q)}{\sqrt{4 (1 + pn) (p + qn) - (n - 2r)^2}}
\]

\[
m = \frac{1}{2} (n + 2).
Special cases. (i.) Suppose \( r/n = \chi \), and \( n \) very large, then

\[
\frac{\bar{m}}{\alpha^2} = \frac{2}{c^2 n (pq - (\frac{1}{2} - \chi)^2)} = \alpha_1, \text{ say},
\]

\[
\frac{\nu}{\alpha} = \frac{(1 - 2\chi)(p - q)}{c (pq - (\frac{1}{2} - \chi)^2)} = \alpha_2, \text{ say}.
\]

Thus we have

\[
y = y_0 e^{-\alpha_0 x - \alpha x^2},
\]

which reduces to the normal type by a change of origin. It is important to notice, however, that the standard deviation of this normal type

\[
= \sqrt{1/2\alpha_1} = \frac{1}{2} c \sqrt{\{n (pq - (\frac{1}{2} - \chi)^2)\}},
\]

and is very different from the value \( c \sqrt{\{(r + 1) pq\}} = \frac{1}{2} c \sqrt{(npq \times 4\chi)} \), nearly, which is the usual form. Only when we put \( p = q = \frac{1}{2} \) and make \( \chi \) small do they agree. We thus conclude: That the normal form may fit a chance distribution, but it does not follow that the standard deviation is of the binomial type generally assumed.

(ii.) Suppose \( \chi = \frac{1}{2} \), corresponding to the withdrawal of one-half of the contents of a vessel, then

\[
y = y_0 (1 + x^2/\alpha_0)^{-\alpha},
\]

where

\[
\alpha_0 = \frac{1}{2} c \sqrt{\{(1 + pm)(1 + qn)\}}.
\]

This is an unlimited and symmetrical frequency curve approaching more and more nearly to the normal form as we increase \( n \). It has, however, a standard deviation

\[
= \frac{1}{2} c \sqrt{(npq)},
\]

while the normal curve would give \( \frac{1}{2} c \sqrt{(npq \times 2)} \).

(iii.) Suppose \( p = q = \frac{1}{2} \), we again reach the form

\[
y = y_0 (1 + x^2/\alpha_0)^{-\alpha},
\]

where

\[
\alpha_0 = \frac{1}{2} c (n + 2) \sqrt{\{1 - (\frac{n - 2\chi}{n + 2})^2\}}.
\]

Make \( n \) infinite and we have again the normal type, but a standard deviation of the form \( \frac{1}{2} c \sqrt{n\chi (1 - \chi)} \), only approaching the usual value when \( \chi \) is small.

We postpone until we have discussed the remaining types the problem of fitting a curve of Type IV. to a series of observations.

(13.) Case II. \( \beta_2 = 4\beta_1\beta_3 \).

Let \( \alpha_1 \) and \( \alpha_2 \) be the roots of \( \beta_1 + \beta_2 x + \beta_3 x^2 = 0 \). Then the curve having the same geometrical relation for its slope is

\[
\frac{d}{dx} \log y = - \frac{x}{\beta_2 (x - \alpha_1) (x - \alpha_2)} = - \frac{1}{\beta_2 (\alpha_1 - \alpha_2)} \frac{d}{dx} \{\alpha_1 \log (x - \alpha_1) - \alpha_2 \log (x - \alpha_2)\},
\]

where
or, if

\[ \frac{1}{\nu} = \beta_0 (a_1 - a_2), \]

\[ y = y_0 (x - a_1)^{-\alpha_1} (x - a_2)^{-\alpha_2}, \]

\[ = y_0 (1 - x/a_1)^{-\alpha_1} (1 - x/a_2)^{-\alpha_2}, \]

by changing constants.

Assuming that \( y_0, \nu, \alpha_1 \) and \( \alpha_2 \) can take any sign whatever, we see that there are three fundamental subtypes of this frequency curve,

(i.) \[ y = y_0 (1 + x/a_1)^{-\alpha_1} (1 - x/a_2)^{-\alpha_2}. \]

This is an asymmetrical curve with limited range and maximum towards mediocrity. As a rule \( \nu a_1 \) and \( \nu a_2 \) are fractional and the curve becomes imaginary beyond the limits \( x = -a_1 \) and \( x = a_2 \).

(ii.) \[ y = y_0 (x/a_1 - 1)^{-\alpha_1} (1 - x/a_2)^{-\alpha_2}. \]

Here the ordinate between \( x = a_1 \) and \( x = a_2 \) varies from infinity to zero, and resembles the frequency curves given by "wealth" distribution or infant mortality.

(iii.) \[ y = y_0 (1 - x/a_1)^{-\alpha_1} (1 + x/a_2)^{-\alpha_2}. \]

This is an asymmetrical curve with limited range, mediocrity being in a minimum. The disappearance of mediocrity is not a very uncommon feature of statistics; the
"prevalence of extremes" may appear not only in meteorological phenomena but in competitive examinations, where the mediocre have occasionally sufficient wisdom to refrain from entering. The type is that of Mr. F. Galton's curve of "consumptivity." 

The curve contains an interesting number of less fundamental subtypes.

(iv.) Make $a_2 = \infty$ in (i),

$$y = y_0 (1 + x/a_1)^{2n} e^{-nx}.$$

This is the limit to the asymmetrical binomial, which has been already referred to in § 8.

(v.) Make $a_1 = a_2$,

$$y = y_0 (1 - x^2/a_1^2)^{2n}.$$

This is the symmetrical frequency curve of limited range.

(vi.) Make $r$ negative in (v),

$$y = \frac{y_0}{(1 - x^2/a_1^2)^{2n}}.$$

This is a symmetrical frequency curve, with limited range, and minimum of mediocrity.

(vii.) Put $r = pa_1$ in (v) and make $a_1 = \infty$,

$$y = y_0 e^{-px}.$$

This is the normal curve.

* 'Natural Inheritance,' 1889, p. 174.
(viii.) Put \( \alpha_2 = \infty \) in (ii.),

\[
y = y_0 \left( \frac{x}{\alpha_1} - 1 \right)^{-\alpha_1} e^{-x}.
\]

This is an asymmetrical frequency curve, with an ordinate varying from \( \alpha_1 \) to \( \infty \) along an infinite range.

All eight of the above types are included in the single form

\[
y = y_0 \left( 1 + \frac{x}{\alpha_1} \right)^{\nu_1} \left( 1 - \frac{x}{\alpha_3} \right)^{\nu_3},
\]
or

\[
y = y_1 x^r (1 - x/c)^s,
\]

if we give positive, negative, or limiting values to the constants. But to do this we require to give values to \( n \) and \( r \) in the expressions for \( \beta_1, \beta_2, \) and \( \beta_3, \) which are not easily intelligible, if we rigidly adhere to our example of drawing a definite quantity of sand from a limited mixture of two kinds of sand. The last type of curve given is, however, the frequency curve for \( \phi \) \( \textit{a priori} \) probabilities, and readily admits of a direct interpretation of the following kind.

Given a line of length \( l, \) and suppose \( r + 1 \) points placed on it at random; what is the frequency with which the point \( pr \) from one end and \( qr \) from the other of the series of \( r + 1 \) points falls on the element \( dx \) of the line?

The answer is clearly

\[
\frac{1}{|p^r| q^r} \left( \frac{x}{l} \right)^r \left( 1 - \frac{x}{l} \right)^s \frac{dx}{l},
\]
or, we have a frequency curve of the type

\[
y = y_0 x^r (1 - x/l)^r.
\]

We may express the problem a little differently. Take \( r + 1 \) cards and slip them at random between the pages of a book, the frequency of the page succeeding the \( pr + 1^{th} \) card is given by the above curve.

* See Crofton, "Probability," § 17, 'Encycl. Brit.'

† The important point to be noticed here is that we are dealing with a distribution in which contributory causes are inter-dependent.
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Until we know very much more definitely than we do at present, how the size of an organ in any individual, say, depends on the sizes of the same organ in its ancestors, or what are the nature of the causes which lead to the determination of prices, or of income, or of mortality at a given age, I do not see that we have any right to select as our sole frequency curve the normal type

\[ y = y_0 e^{-yz} \]

in preference to the far more general

\[ y = y_0 (1 + x/a_1)^{m_1} (1 - x/a_2)^{m_2}, \]

which not only includes the former, but supplies the element of skewness which is undoubtedly present in many statistical frequency distributions. As we may look upon the former as a limit to a coin-tossing series, so the latter represents a limit to teetotum-spinning and card-drawing experiments. It is not easy to realise why nature or economics should, from the standpoint of chance, be more akin to tossing than to teetotum-spinning or card-dealing. At any rate, from purely utilitarian and prudent motives, we are justified so long as the analysis is manageable, in using the more general form. It will always give us a measure of the divergence of particular statistics from the normal type, and in many cases of skew frequency, it can be used when it would be the height of absurdity to apply the normal curve at all.

Since Types I., II., III., and V. are all represented by the curve

\[ y = y_0 (1 + x/a_1)^{m_1} (1 - x/a_2)^{m_2} \]

and Type IV. by the curve

\[ y = y_0 \frac{1}{(1 + x^2/a^2)^{m}} e^{-x^2/a^2}, \]

we have only to deal with these two cases in general. We shall refer, in the course of our work, to special simplifications arising in particular sub-cases. After a description of the manner in which these generalised probability curves may be fitted to statistics, we shall indicate, by examples, their practical applications.

(14.) On the Generalised Probability Curve. Type I.

\[ y = y_0 (1 + x/a_1)^{m_1} (1 - x/a_2)^{m_2}. \]

Let the range \( a_1 + a_2 = b \); let \( m_1 = \nu a_1, \quad m_2 = \nu a_2, \quad z = (a_1 + x)/(a_1 + a_2) \), whence \( x = -a_1, \quad z = 0 \) and \( z = a_2, \quad z = 1 \).

Further let

\[ \eta = y_0 \frac{(a_1 + a_2)^{m_1 + m_2}}{a_1^{m_1} a_2^{m_2}}, \]

\[ = y_0 \frac{m_1 + m_2}{m_1^{m_1} m_2^{m_2}}, \]

thus

\[ y = \eta z^m (1 - z)^{m_2}. \]
Let \( \alpha \) be the area of the curve between \( x = -a_1 \) and \( x = a_2 \). \( \alpha \mu_n' \) its \( n^{th} \) moment round a parallel to the axis of \( y \) through \( x = -a_1 \), and \( \alpha \mu_n \) its \( n^{th} \) moment round the centroid vertical.

Then we have

\[
\alpha \mu_n' = \int_0^b y^2 x^n \, dx, \\
= b^{n+1} n \int_0^1 z^{m_1+n}(1 - z)^{m_2} \, dz, \\
= b^{n+1} n B(m_1 + n + 1, m_2 + 1), \\
= b^{n+1} n \Gamma(m_1 + n + 1) \Gamma(m_2 + 1) \Gamma(m_1 + m_2 + n + 2).
\]

Thus, by the fundamental property of the \( \Gamma \) function, we have

\[
\alpha = b\eta \Gamma(m_1 + 1) \Gamma(m_2 + 1) / \Gamma(m_1 + m_2 + 2), \\
\mu'_1 = \frac{b(m_1 + 1)}{m_1 + m_2 + 2}, \\
\mu'_2 = \frac{b^2(m_1 + 2)(m_1 + 1)}{(m_1 + m_2 + 3)(m_1 + m_2 + 2)}, \\
\mu'_3 = \frac{b^2(m_1 + 3)(m_1 + 2)(m_1 + 1)}{(m_1 + m_2 + 4)(m_1 + m_2 + 3)(m_1 + m_2 + 2)}, \\
\mu'_4 = \frac{b^2(m_1 + 4)(m_1 + 3)(m_1 + 2)(m_1 + 1)}{(m_1 + m_2 + 5)(m_1 + m_2 + 4)(m_1 + m_2 + 3)(m_1 + m_2 + 2)}.
\]

From these we easily deduce by the formula connecting \( \mu \) and \( \mu' \), if we write for brevity, \( m_1 + 1 = m'_1 \), \( m_2 + 1 = m'_2 \), and \( m'_1 + m'_2 = r' \):

\[
\mu_2 = \frac{b^2 m'_1 m'_2}{r^2(r + 1)}, \\
\mu_3 = \frac{2b^3 m'_1 m'_2}{r^3(r + 1)(r + 2)}, \\
\mu_4 = \frac{3b^4 m'_1 m'_2}{r^4(r + 1)(r + 2)(r + 3)}.
\]

Now, \( \alpha, \mu_2, \mu_3, \) and \( \mu_4 \) are to be found by the methods indicated in Art. 4 from the polygon of observations, and may be supposed known quantities, when we are dealing with the fitting of frequency-curve to observations.

Then, if \( \beta_2 = \mu_3/\mu_2^3 \), and \( \beta_1 = \mu_2^2/\mu_3^3 \), \( \epsilon = m'_1 m'_2 \), we have:

\[
\beta_1 = \frac{4(r^2 - 4\epsilon)}{\epsilon(r + 1)} , \\
\beta_2 = \frac{3(r + 1)(2r^3 + \epsilon(r - 6))}{\epsilon(r + 2)(r + 3)}
\]

Thus:

\[
\frac{\beta_1 (r + 2)^2}{4(r + 1)} = \frac{r^2}{\epsilon} - 4, \\
\frac{\beta_2 (r + 2)(r + 3)}{3(r + 1)} = \frac{2r^3}{\epsilon} + r - 6.
\]

whence, eliminating \( r^2/\epsilon \), we find:

\[
r = \frac{6(\beta_2 - \beta_1 - 1)}{3\beta_1 - 2\beta_2 + 6}.
\]
This gives \( r \), then:

\[
\epsilon = \frac{r^2}{4 + \frac{1}{2} \beta_1 (r + 2)^2 (r + 1)},
\]

\[
b^2 = \frac{\mu_2 r^2 (r + 1)}{\epsilon} = \mu_2 \beta_1 (r + 2)^2 + 16 (r + 1),
\]

or

\[
b = \sqrt{\frac{\mu_2 \{\beta_1 (r + 2)^2 + 16 (r + 1)\}}{2}}.
\]

Since

\[
r = m_1' + m_2', \quad \epsilon = m_1' m_2',
\]

\( m_1' \) and \( m_2' \) are roots of

\[
m'^2 - rm' + \epsilon = 0.
\]

Thus \( m_1 = m_1' - 1 \) and \( m_2 = m_2' - 1 \) are determined.

Further, \( a_1 + a_2 = b, \quad a_1/a_2 = m_1/m_2, \) and \( \nu = m_1/a_1 \) are all determined.

Lastly:

\[
y_0 = \eta \frac{m_1 m_2}{(m_1 + m_2)^{m_1 + m_2}},
\]

and

\[
a = b \eta \frac{\Gamma (m_1 + 1) \Gamma (m_2 + 1) / \Gamma (m_1 + m_2 + 2)},
\]

give:

\[
y_0 = \frac{a}{b} \frac{m_1 m_2}{(m_1 + m_2)^{m_1 + m_2}} \frac{\Gamma (m_1 + 2) \Gamma (m_2 + 2)}{\Gamma (m_1 + 1) \Gamma (m_2 + 1)},
\]

which completes the solution,\(^*\) if a Table of \( \Gamma \) functions is to hand.

Remarks.—It is clear that the solution is unique.

It is necessary in order that the solution may be real, that \( m_1' \) and \( m_2' \) should be real or \( r^2 > 4 \epsilon \). Hence, if \( \epsilon \) be negative, there is certainly a solution, because \( r \) is always real. The solution forms, however, one of the sub-types referred to in our Art. 13, (ii) and (iii).

If \( \epsilon \) be positive, we must have \( r^2/\epsilon - 4 \) positive, or

\[
\frac{\beta_1 (3 + \beta_2)^2}{(6 + 3 \beta_1 - 2 \beta_2) (4 \beta_2 - 3 \beta_1)} > 0.
\]

Now it is easy to prove that for any curve \( 4 \beta_2 - 3 \beta_1 \) or \( 4 \mu_1 \mu_2 - 3 \mu_3 \) is positive, for \( \mu_1, \mu_2 \) is always greater than \( \mu_2 \).

Thus, we must have

\[
6 + 3 \beta_1 - 2 \beta_2 > 0,
\]

or

\[
2 \mu_2 (3 \mu_2^2 - \mu_4) + 3 \mu_3^2 > 0.
\]

\(^*\) Very often with sufficient accuracy we may take:

\[
y_0 = \frac{a}{b} \frac{(m_1 + m_2 + 1) \sqrt{(m_1 + m_2)} \frac{1}{6} \left( \frac{1}{m_1 + m_2} - \frac{1}{m_2} - \frac{1}{m_1} \right)}{\sqrt{(2 \pi m_1 m_2)}}.
\]
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Now it is theoretically impossible to fit a normal curve \((\mu_1 = 3\mu_2^3)\) to a frequency distribution for which \(\mu_4 > 3\mu_2^3\). It is, however, possible to fit this generalised curve of Type I, although \(\mu_4 > 3\mu_2^3\), provided there is sufficient skewness to render

\[3\mu_2^3 > 2\mu_2 (\mu_4 - 3\mu_2^3).\]

Hence the first stage in determining the type of curve suitable for a given set of observations is to ascertain the value of

\[2\mu_2 (3\mu_2^3 - \mu_4) + 3\mu_2^2.\]

If this expression be positive, we see that a limited range of variation is a possibility.

Passing from range to skewness we remark that the distance \(d\) between the centroid vertical and the maximum ordinate

\[= a_4 - \mu_1 = a_4 - bm_1/(m_1' + m_2'),\]

\[= a_2m_2 - a_2m_1'

\[m_1' + m_2']\]

\[= \frac{b (m_1 - m_2)}{(m_1 + m_2) (m_1 + m_2 + 2)}.\]

Now it might seem that \(d/b\) would form a good measure of skewness, and it would be so if all curves had a limited range. But, as they have not, it seems to me better to take as the measure of skewness the ratio of the distance between the maximum ordinate and the centroid to the length of the swing radius of the curve about the centroid vertical, i.e., the quantity \(d/\sqrt{\mu_2}\).

In our case we have accordingly,

\[
\text{skewness} = \frac{m_1 - m_2}{m_1 + m_2} \sqrt{\left(\frac{m_1 + m_2 + 3}{(m_1 + 1)(m_2 + 1)}\right)},
\]

\[= \frac{1}{2} \sqrt{\beta_1 \frac{r + 2}{r - 2}},\]

in our previous notation.*

Thus range and skewness are determined in Type I.

(15.) A very considerable simplification of the above analysis arises when the range is given by the conditions of the problem itself, e.g., guessing between two given tints. In this we only require the moments \(\mu_1'\) and \(\mu_2'\) about one end of the range, and the solution becomes as easy as in the case of fitting a normal curve.

Since \(b, \mu_1'\) and \(\mu_2'\) are known, let

\[\gamma_1 = \mu_1'/b\quad \text{and} \quad \gamma_2 = \mu_2'/\mu_1'b.\]

* The points of inflexion of the curve are at distances \(\pm \sqrt{a_1a_2/(m_1 + m_2 - 1)}\) on either side of the maximum ordinate.
Then
\[
\gamma_1 = \frac{m'_1}{m'_1 + m'_2}, \quad \gamma_2 = \frac{m'_1 + 1}{m'_1 + m'_2 + 1},
\]
and we have at once
\[
m'_1 = \frac{\gamma_1\left(\gamma_2 - 1\right)}{\gamma_1 - \gamma_2}, \quad m'_2 = \frac{\left(\gamma_2 - 1\right)\left(1 - \gamma_1\right)}{\gamma_1 - \gamma_2}.
\]

Then \(\alpha_1/\alpha_2 = (m'_1 - 1)/(m'_2 - 1)\), and \(\alpha_1 + \alpha_2 = b\) give \(\alpha_1\) and \(\alpha_2\). Finally \(y_0\) is given as before by
\[
y_0 = \frac{\alpha}{b} \frac{m_{1\sigma}^n m_{2\sigma}^n}{(m_1 + m_2)^{m_1 + m_2}} \frac{\Gamma(m_1 + m_2 + 2)}{\Gamma(m_1 + 1) \Gamma(m_2 + 1)}.
\]

(16.) A perhaps still more interesting and usual case arises when one end of the range is given, i.e., when \(\mu'_1\), but not \(b\), is known. For example, a curve of distribution of disease with age, the liability to the disease starting with birth. Here we require to calculate from the observations \(\alpha_1\mu'_1, \mu'_2\) and \(\mu'_3\). The solution is as follows:

Let
\[
\mu'_2/\mu'_1 = x_2, \quad \mu'_3/\mu'_2 = x_3;
\]
then
\[
x_3 = \frac{(m'_1 + 1)\left(m'_1 + m'_2\right)}{m'_1\left(m'_1 + m'_2 + 1\right)} = \frac{1 + \nu}{1 + \nu'},
\]
\[
x_3 = \frac{(m'_1 + 2)\left(m'_1 + m'_2\right)}{m'_1\left(m'_1 + m'_2 + 2\right)} = \frac{1 + 2\nu}{1 + 2\nu'}.
\]

If \(\nu = 1/m_1'\) and \(\nu = 1/(m_1' + m_2')\).

Solving
\[
u = \frac{1 + x_3 - 2x_3}{2(x_3 - x_3)}, \quad \nu = \frac{2x_3 - x_3 - x_3 x_3}{2(x_3 - x_3)}.
\]

Thus,
\[
m'_1 = \frac{2(x_3 - x_3)}{2x_3 - x_3 - x_3 x_3}, \quad m'_2 = \frac{2(x_3 - x_3)(x_3 - 1)(1 - x_3)}{(1 + x_3 - 2x_3)(2x_3 - x_3 - x_3 x_3)},
\]
\[
b = \mu'_1 \left(m'_1 + m'_2\right)/m'_1 = \mu'_1 \nu/\mu
\]
\[
= \mu'_1 \frac{2x_3 - x_3 - x_3 x_3}{2(x_3 - x_3)},
\]
determines the range.

Hence, since
\[
\alpha_1 + \alpha_2 = b, \quad \alpha_1/\alpha_2 = \frac{m'_1 - 1}{m'_2 - 1},
\]
we have, with the aid of the previous expression for \(y_0\), the complete solution of the problem.
(17.) Generalised probability curve of Type II. Limited Range and Symmetry.

\[ y = y_0 \left(1 - \frac{x^2}{\sigma^2}\right)^m. \]

The solution in this case follows very easily from (14) by putting \( \beta_1 = 0 \), we have at once

\[ 2(m + 1) = \frac{\beta_3}{2 - \beta_3} \]

or

\[ m = \frac{5\beta_3 - 9}{2(3 - \beta_3)} = \frac{5\mu_4 - 9\mu_2^2}{2(3\mu_3^2 - \mu_4)}. \]

Since \( \mu_2 = \frac{b\epsilon}{2(r + 1)} \), and clearly \( \epsilon = r^2/4 \),

we have

\[ b = 2a = 2\sqrt{\mu_2(r + 1)}, \]

or

\[ a = \frac{\sqrt{2\mu_3\beta_3}}{\sqrt{3 - \beta_3}} = \frac{\sqrt{2\mu_2\mu_4}}{\sqrt{3\mu_3^2 - \mu_4}}. \]

Finally

\[ y_0 = \frac{a}{b} \frac{m^{2m}}{(2m)!} \frac{\Gamma(2m + 2)}{(m + 1)^3} \]

\[ = \frac{a}{b} \frac{\sqrt{3 - \beta_3}}{2\sqrt{2\mu_3\beta_3}} \frac{(2m + 2)}{\Gamma(2m + 1)^3} \]

\[ = a \frac{\sqrt{3\mu_3^2 - \mu_4}}{2\mu_3\mu_4} \frac{\Gamma(m + 2)}{2^{m+1}\Gamma(m + 1)^3} \]

\[ = a \frac{\sqrt{3\mu_3^2 - \mu_4}}{2\mu_3\mu_4} \frac{\Gamma(m + 1.5)}{\sqrt{\pi}\Gamma(m + 1)}. \]

For the normal frequency curve \( \mu_4 = 3\mu_3^2 \), for a symmetrical point-polygon \( 3\mu_3^2 > \mu_4 \).

Hence, whenever a symmetrical frequency curve differs from the normal curve on the side of the point-binomial, we can better the normal solution by taking a symmetrical frequency curve of limited range.

Since

\[ y = y_0 \left(1 - \frac{x^2}{\sigma^2}\right)^m, \]

and

\[ \frac{m}{\sigma^2} = \frac{5\beta_3 - 9}{4\mu_3\beta_3} = \frac{1}{2\mu_3}, \]

if \( \beta_3 = 3 \), we easily trace the transition from the limited symmetrical curve to the normal curve with infinite range.

Quite apart from the extremely interesting problem of finding the range, it is clear that better fits will be obtained for symmetrical distributions by the aid of this limited range curve for all cases in which \( 3\mu_3^2 > \mu_4 \).
Generalised Probability Curve of the Type III. Range limited in one direction only.

\[ y = y_0 (1 + x/a)^p e^{-xz}. \]

In this case we have no need to determine the value of \( \mu_4 \), and the analysis is much simplified by the replacement of the B function by a single \( \Gamma \) function.

Take \( z = \gamma (a + x) \) and write \( \gamma a = p \), we have

\[ y = \frac{y_0 p^p}{p^p} z^p e^{-z}. \]

Further, \( x = -a, z = 0, x = \infty, z = \infty \). Thus we find

\[ \alpha \mu'_n = \int_{-\infty}^{\infty} y (x + a)^n dx = \frac{y_0 p^p}{p^{p+1}} \int_{0}^{\infty} z^{p+n} e^{-z} dz. \]

Hence

\[ \alpha = \frac{y_0 p^p}{p^{p+1}} \Gamma (p + 1), \quad \alpha \mu'_n = \frac{\alpha \Gamma (p + n + 1)}{\gamma^n \Gamma (p + 1)}, \]

whence

\[ \mu'_1 = \frac{p + 1}{\gamma}, \quad \mu'_2 = \frac{(p + 1)(p + 2)}{\gamma^2}, \]
\[ \mu'_3 = \frac{(p + 1)(p + 2)(p + 3)}{\gamma^3}, \quad \mu'_4 = \frac{(p + 1)(p + 2)(p + 3)(p + 4)}{\gamma^4}. \]

Or, transposing to the centroid-vertical, we have

\[ \mu_2 = \frac{p + 1}{\gamma^2}, \quad \mu_3 = \frac{2(p + 1)}{\gamma^3}, \quad \mu_4 = \frac{3(p + 1)(p + 2)}{\gamma^4}. \]

The first two results give us at once

\[ \gamma = 2\mu_2/\mu_3, \quad \rho = 4\mu_2^2/\mu_3^2 - 1, \]

whence

\[ \alpha = \frac{\rho}{\gamma} = \frac{2\mu_2^2}{\mu_3^2} - \frac{\mu_3}{2\mu_2}, \quad y_0 = \frac{\alpha}{\alpha \phi \Gamma (p + 1)}. \]

This completes the solution of the problem, which is seen to require only the determination of \( \mu_2 \) and \( \mu_3 \).

Remarks.—The distance \( d \) of the centroid-vertical from the axis of \( y \) or maximum ordinate \( d \), is given by

\[ d = \mu_1 - a = 1/3\mu_3/\mu_2. \]

Thus

\[ \text{skewness} = d/\sqrt{\mu_2} = 1/3\mu_3/\mu_2. \]
If we transfer the origin to the centroid-vertical we have

\[ y = y_1 \left(1 + \frac{x}{2\mu_3^2/\mu_4}\right)^{\mu_2^2/\mu_3^{2}-1} e^{-2\mu_4/\mu_3} \]

where

\[ y_1 = \frac{x}{\sqrt{(2\pi\mu_2)}} \sqrt{\frac{2\pi (p + 1)}{e^{-(p+1)(p+1)}}} \]

It is interesting to note how this skew curve passes into the normal curve when \( \mu_3 \) is made vanishingly small, or \( p = \infty \).

By Wallis's theorem the limit to \( y_1 = \frac{a}{\sqrt{2\pi\mu_2}} \).

It remains to find the limit of

\[ \left(1 + \frac{x}{2\mu_3^2/\mu_4}\right)^{\mu_2^2/\mu_3^{2}-1} e^{-2\mu_4/\mu_3} = \left(1 + \frac{1}{\sqrt{(p + 1)} \sqrt{(\mu_2)}}\right)^{\mu_2^2/\mu_3^{2}} e^{-\sqrt{p + 1} \sqrt{\mu_2}} \]

\[ = \left[\left(1 + u\right) e^{-\frac{1}{2}}\right]_{u=0} \]

Now the limit of \( \{(1 + u) e^{-u}\}^{1/a} \) for \( u = 0 \) is easily found to be \( e^{-\frac{1}{2}} \), hence

\[ y = ae^{-\sigma^2/\mu_2} \sqrt{(2\pi\mu_2)} \]

the normal form.

Returning to the value we have found for \( \mu_4 \) and eliminating \( p \) and \( \gamma \) between \( \mu_2 \), \( \mu_3 \), and \( \mu_4 \) we find

\[ 2\mu_2 \left(3\mu_3^2 - \mu_4\right) + 3\mu_3^2 = 0. \]

This is the expression (see p. 398) which must be positive in the case of limited range. It is zero also for the normal curve, because both \( 3\mu_3^2 - \mu_4 \) and \( \mu_3 \) vanish. Hence the more nearly the quantity \( 2\mu_2 \left(3\mu_3^2 - \mu_4\right) + 3\mu_3^2 \) approaches to zero, the more nearly are we able to fit our statistics with a skew frequency-curve having a range limited in one direction only.

(18 bis).—The skew frequency-curve of Type III. deserves especial notice. It is intermediate between those of Type I. and Type IV., and they differ very little from it in appearance. Hence, if the reader has once studied the various forms which Type III. can take as we alter its constants, he will grasp at once the forms taken by Types I. and IV., by simply considering the range doubly limited or doubly unlimited. To assist the process of realising Type III., Plate 9, fig. 5, has been constructed; it contains seven sub-types of this species, varying from fig. 1., in which the curve is asymptotic to the maximum frequency-ordinate to fig. 7., which is practically identical with the normal curve. Taking \( y = y_0 \left(1 + x/a\right)^{\nu} e^{-\gamma x} \) for the equation to the curve, we have the following values for the constants \( p_1 \) and \( \gamma' :-
In the diagrams vertical and horizontal scales \((y_0\) and \(a\)) have been chosen so as to illustrate best the changes of shape in the curve. The general correspondence of this series with actual types of frequency curve, as indicated in Plate 7, fig. 1, will at once strike the reader.

The mean, the median, and the mode or maximum-ordinate are marked by \(bb\), \(cc\), and \(aa\), respectively, and as soon as the curves were drawn, a remarkable relation manifested itself between the position of these three quantities: the median, so long as \(p\) was positive, was seen to be about one-third from the mean towards the maximum. For \(p\) negative and between 0 and \(-1\), this relation was not true. The distance between the maximum-ordinate and the mean is, if the equation to the curve be

\[ y = y_0 x^p e^{-yx}, \]

equal to \(1/\gamma\). Now the maximum cannot be accurately determined from observation, but a fair approximation can be made to the median. Hence the constant \(\gamma\) could, if the above graphical relation were shown to be always true, be determined approximately as the inverse of thrice the distance between median and mean.

Now distance of mean from origin = \((p + 1)/\gamma\),
and " maximum " = \(p/\gamma\).

Hence, supposing distance of median = \((p + c)/\gamma\), we should expect to find \(c = 2/3\) about.

Equating the integral which gives the area up to the median to half the total area, we have

\[ y_0 \int_{p+c}^{\gamma} x^p e^{-yx} \, dx = \frac{1}{2} y_0 \int_{0}^{\gamma} x^p e^{-yx} \, dx, \]

or,

\[ \int_{p+c}^{\gamma} z^p e^{-z} \, dz = \frac{1}{2} \int_{0}^{\gamma} z^p e^{-z} \, dz. \]

This is the equation for \(c\). Unable to solve it generally I gave \(p\) a series of integer values and found in all cases \(c\) nearly \(-67\). Its value, however, decreased as \(p\)
increased. I, therefore, assumed \( c \) to be really of the form \( c = c_1 + \frac{c_2}{p} \), and determining \( c_1 \) and \( c_2 \) by the method of least squares, found

\[
c = 0.6691 + 0.0094/p.
\]

Probably this is only the beginning of a rapidly converging series in inverse powers of \( p \), but it would appear to suffice for most practical purposes. It is only true for \( p > 1 \) and does not explain why, when \( p \) is positive and fractional, \( c \) is still apparently near \( \frac{3}{4} \); thus its value for \( p = 0 \) has only risen to 0.6931. We have then the following fairly simple means of determining roughly the constants of a skew curve of this type:

1. Find the mean and the median; these give \( \gamma \), approximately.
2. Find \( \mu_2 \) for the mean; this gives \( p \), since \( \mu_2 = \frac{(p + 1)}{\gamma^2} \).
3. Knowing \( p \), correct the value of \( \gamma \) by using the above value for \( c \), and so obtain a corrected \( p \).
4. Determine \( y_0 \) from the area.

This method is not very laborious and may be of service in some cases. It will, of course, fail for any curves in which \( p \) is negative, and must only be applied when the curve is known to be of Type III. If the beginning of the range is definitely known, we may save stage (2) above and find \( p \) from the distance of the mean from the start of the range.

(19.) Generalised Probability Curve of Type IV. Range unlimited, but form skew.

\[
y = \frac{y_0}{\{1 + (x/a)^2\}^{1/4}} e^{-v \tan^{-1}(x/a)}.
\]

Put \( x = \alpha \tan \theta \), hence

\[
y = y_0 \cos^{2n} \theta e^{-v \theta}.
\]

\[
\alpha \mu_n = \int_{-\infty}^{\infty} x^n e^x dx = y_0 \omega^{n+1} \int_{-\pi/2}^{\pi/2} \cos^{2n-2}\theta \sin^n \theta e^{-\theta} d\theta,
\]

\[
= y_0 \omega^{n+1} \int_{-\pi/2}^{\pi/2} \cos^{n-2}\theta \sin^n \theta e^{-\theta} d\theta, \text{ if } r = 2m - 2,
\]

\[
= \frac{y_0 \omega^{n+1}}{r - n + 1} \left\{ (n-1) \int_{-\pi/2}^{\pi/2} \cos^{n-2}\theta \sin^{n-2}\theta e^{-\theta} d\theta - \int_{-\pi/2}^{\pi/2} \cos^{r-1}\theta \sin^{r-1}\theta e^{-\theta} d\theta \right\}
\]

\[
= \frac{\alpha}{r - n + 1} \left\{ (n-1) \alpha \mu_{n-2} - \nu \mu_{n-1} \right\} \alpha,
\]

provided \( r > n - 1 \).

* The points of inflexion may also occasionally be found from the observations; they are at distances \( \pm \sqrt{p/\eta} \) on either side of the maximum ordinate.
Thus, if we know $\alpha$ and $\mu_1$, we can find the successive $\mu$'s. Now

$$\alpha = y_0 e^{\int_{-\pi/2}^{\pi/2} \cos \theta e^{-\nu \theta} d\theta},$$

$$= y_0 e^{-\nu \int_{0}^{\pi} \sin \theta e^{+\nu \theta} d\theta},$$

and depends on the integral $\int_{0}^{\pi} \sin \theta e^{+\nu \theta} d\theta$, which I propose to write $G(\nu)$.

The result above for $\mu_1$ shows us that the more general integral $\int_{0}^{\pi} \cos \theta \sin^2 \theta e^{+\nu \theta} d\theta$ can always be expressed in terms of $G$-functions. Further:

$$a \mu_1 = y_0 e^{\int_{-\pi/2}^{\pi/2} \cos^{r-1} \theta \sin \theta e^{-\nu \theta} d\theta},$$

$$= - y_0 e^{\int_{-\pi/2}^{\pi/2} \cos \theta e^{-\nu \theta} d\theta} = - \frac{\alpha \nu}{\nu}.\]

Thus we find by the formula of reduction above:

$$\mu' = \frac{\alpha^2}{r (r - 1)} (r + \nu^2), \quad \mu' = - \frac{\alpha \nu}{r (r - 1)(r - 2)} (3r - 2 + \nu^2),$$

and

$$\mu' = \frac{\alpha^2}{r (r - 1)(r - 2)(r - 3)} \left\{3r (r - 2) + \nu^2 (6r - 8) + \nu^4\right\}.$$

Referring to centroid vertical, we have:

$$\mu_5 = \frac{\alpha^2}{r^2 (r - 1)} (r^2 + \nu^2), \quad \mu_3 = - \frac{\alpha \nu}{r^3 (r - 1)(r - 2)} \left\{3r (r - 2) + \nu^2 (6r - 8) + \nu^4\right\},$$

$$\mu_4 = \frac{3 \alpha^2 (r^2 + \nu^2)}{r^4 (r - 1)(r - 2)(r - 3)} \left\{(r + 6) (r^2 + \nu^2) - 8 \nu^2\right\}.$$

These may be rewritten, if $z = r^2 + \nu^2$,

$$\mu_5 = \frac{\alpha^2 z}{r^2 (r - 1)}, \quad \mu_3 = - \frac{4 \alpha \nu \sqrt{(z - r^2)}}{r^3 (r - 1)(r - 2)},$$

$$\mu_4 = \frac{3 \alpha^2 \{r + 6}z - 8 \nu^2\} \{r + 6\} (r - 1)(r - 2)(r - 3).

As before, putting $\beta_1 = \mu_5^2 / \mu_3^2$ and $\beta_2 = \mu_4 / \mu_3^2$, we have

$$\frac{\beta_1 (r - 2)^2}{2 (r - 1)} = \frac{8}{z} \frac{\nu^2}{z} = 8,$$

$$\frac{\beta_2 (r - 2) (r - 3)}{3 (r - 1)} = r + 6 - 8 \frac{\nu}{z}.$$
Adding and dividing out by \( r - 2 \), we have
\[
r = \frac{6 (\beta_2 - \beta_1 - 1)}{2\beta_2 - 3\beta_1 - 6},
\]
hence
\[
m = \frac{1}{2} (r + 2)
\]
is known. Further
\[
z = \frac{r^2}{1 - \frac{\beta_1 (r - 2)^2}{16 r - 1}}
\]
is known, whence
\[
v = \sqrt{(z - r^2)}
\]
is given. Finally
\[
a = r \sqrt{\left(\frac{\mu_2 (r - 1)}{z}\right)}
\]
and
\[
y_0 = \frac{\alpha e^{\lambda r}}{\alpha \int_0^\pi \sin \theta e^{\lambda \theta} d\theta}
\]
completely determine the problem.

Remarks. The solution is clearly unique.

(i.) To determine the skewness we must find the position of the ordinate for which \( dy/dx = 0 \); this is \( x_0 = -\frac{v\alpha}{2m} = -\frac{v\alpha}{r + 2} \).

But
\[
d = -\mu_1' + x_0 \frac{v\alpha}{r} - \frac{v\alpha}{r + 2} = \frac{2v\alpha}{r (r + 2)}.
\]
Hence
\[
\text{skewness} = \frac{d}{\sqrt{\mu_2}} = \frac{2v}{r + 2} \sqrt{\left(\frac{r - 1}{r^2 + v^2}\right)} = \frac{1}{2} \sqrt{\beta_1} \frac{r - 2}{r + 2} \quad (\text{cf. p. 370}).
\]

(ii.) We further notice that
\[
r - 1 = \frac{4\beta_2 - 3\beta_1}{2\beta_2 - 3\beta_1 - 6}.
\]
Hence, since \( 4\beta_2 \) is always \( > 3\beta_1 \) (see p. 369), it follows, since \( r > 1 \), that we must have
\[
2\beta_2 - 3\beta_1 - 6 > 0,
\]
or
\[
2\mu_2 (3\mu_2^2 - \mu_4) + 3\mu_3^2 < 0.
\]

* Whether we give \( v \) the \(-\) or \(+\) sign will depend upon the sign of \( \mu_3 \) in the actual statistics.
Thus this expression is again critical for the class of curve with which we are dealing. We may say that a skew frequency curve will have limited range, range limited in one direction only, or unlimited range according as

$$2\mu_2 (3\mu_3^2 - \mu_4) + 3\mu_3^2$$

is greater than, equal to or less than zero. Thus the calculation of this expression is the first step towards the classification of a frequency curve given by observation.

(iii.) It is noteworthy that the values we have obtained for \( r, z, \alpha, \nu \) and \( y_0 \) will be real and possible if \( r > 1 \). On the other hand we have required in our work that \( r \) should be \( \geq 3 \). I propose now to return to this point. So long as \( r > 1 \) the values of both \( \mu'_1 \) and \( \mu_2 \) will be finite, but the values of \( \mu'_3 \) and \( \mu'_4 \) and consequently of \( \mu_3 \) and \( \mu_4 \) will be infinite if \( r \) be \( < 3 \). That is to say, the third and fourth moments of the curve about the centroid vertical become infinite. This is quite conceivable from the geometrical standpoint, and various interesting questions, of purely theoretical value however, arise according as \( r > 1 \) and \( < 2 \), i.e., \( \mu_4 \) and \( \mu_3 \) are both infinite, or \( r > 2 \) and \( < 3 \), i.e., \( \mu_4 \) alone is infinite. The solution we have given fails in these cases. We should obtain, however, finite relations between the four constants of the equation to the curve by taking the first and second moments \( \alpha \mu''_1 \) and \( \alpha \mu''_2 \) round the axis of \( x \); we find in this case

$$\alpha \mu''_1 = \frac{1}{2} y_0^2 \alpha \int_{-\pi/2}^{\pi/2} \cos^{\nu+2} \theta e^{-2\nu \theta} d\theta,$$
$$\alpha \mu''_2 = \frac{1}{3} y_0^2 \alpha \int_{-\pi/2}^{\pi/2} \cos^{\nu+4} \theta e^{-2\nu \theta} d\theta,$$

or,

$$\mu''_1 = \frac{1}{2} y_0 e^{-2\nu} G (2r + 2, 2\nu)/G (r, \nu),$$
$$\mu''_2 = \frac{1}{3} y_0^2 e^{-2\nu} G (3r + 4, 3\nu)/G (r, \nu).$$

These results together with

$$\mu_2 = \frac{\alpha^2 (r^2 + \nu^2)}{r^2 (r - 1)}, \quad \alpha = y_0 e^{-\nu} G (r, \nu),$$

are theoretically sufficient to determine the four constants \( r, \nu, y_0 \) and \( \alpha \). Practically they would hardly be of service without very elaborate tables of the \( G \) functions.

As a matter of fact, we are very unlikely in dealing with actual statistics to meet with cases in which \( \mu_3 \) and \( \mu_4 \) become infinite, because neither the range of observations, nor the size of the groups observed at great distances from the origin can be infinite. With finite values of \( \mu_3 \) and \( \mu_4 \), it is, however, easy to see that we always obtain from our solution on page 377 a value of \( r > 3 \), so that the solution is self-consistent.
(iv.) It remains to say a few words about the integral

$$G(r, \nu) = \int_{0}^{r} \sin^3 \theta e^\nu d\theta.$$  

Provided \( r > 1 \), we find a formula of reduction

$$G(r, \nu) = \frac{r(r - 1)}{r^3 + \nu^3} G(r - 2, \nu).$$

Thus the value of the integral from \( r = 0 \) to \( r = 2 \) only will be required for diverse values of \( \nu \). The integral does not yet appear to have been studied at length or tabulated. Dr. A. R. Forsyth has kindly answered my inquiry for a fairly easy method of reducing \( G(r, \nu) \) for purposes of calculation, by sending me the formula

$$G(r, \nu) = \frac{2^{-\nu} \pi \nu^\nu \Pi(r)}{\Pi(\frac{1}{2}r - \frac{1}{2}\nu i) \Pi(\frac{1}{2}r + \frac{1}{2}\nu i)},$$

where \( \Pi \) is Gauss’s function such that

$$\Pi(n) = \Gamma(n + 1).$$

Taking as definition of \( \Pi \) that

$$\Pi(z) = \lim_{n \to \infty} \frac{1 \cdot 2 \cdot \ldots \cdot n}{(z + 1)(z + 2)\ldots(z + n)} n^z$$

when \( n \) is infinite, we can reduce the above expression to the form

$$G(r, \nu) = \frac{2^{-\nu} \pi \nu^\nu \Gamma(r + 1)}{\text{Product}_{n=1}^{\infty} \left(1 + \frac{\nu^2 + \nu^3}{4n^2(1 + r/n)}\right)}.$$

Here, since \( r \) can always be supposed to lie between 0 and 2, when \( \nu \) is small a few terms of the product will generally suffice for the calculation of \( G(r, \nu) \) to the degree of accuracy required in statistical practice.

On the other hand when \( r \) is large, i.e., generally in cases of slight skewness, I find if \( \tan \phi = \nu/r \)

$$\Pi\left(\frac{1}{2}r - \frac{1}{2}\nu i\right) \Pi\left(\frac{1}{2}r + \frac{1}{2}\nu i\right) = \frac{\pi^r}{\cos \phi} e^{-\nu} e^{-\nu} \left(\frac{\nu}{2 \cos \phi}\right) e^\nu \cos \frac{\phi}{2} - \frac{\nu \tan \phi}{2}$$

very nearly.

Hence

$$y_0 = \frac{a}{a} \sqrt{\frac{\cos \phi}{2\pi} \left(\frac{\cos \phi}{2}\right)^{-\nu + 1}}$$

very nearly.

(20.) We have now considered methods for fully investigating whether a given system of measurements has a limited range, and for ascertaining the degree of skewness of the system. Analytically, our work may be expressed as follows:—

The slope of the normal curve is given by a relation of the form

$$\frac{1}{y} \frac{dy}{dx} = -\frac{x}{c_1}.$$ 

The slope of the curve correlated to the skew binomial as the normal curve to the symmetrical binomial is given by a relation of the form

$$\frac{1}{y} \frac{dy}{dx} = -\frac{x}{c_1 + c_2 x}.$$ 

Finally, the slope of the curve correlated to the hypergeometrical series (which expresses a probability distribution in which the "contributory causes" are not independent, and not equally likely to give equal deviations in excess and defect) as the above curves to their respective binomials is given by a relation of the form

$$\frac{1}{y} \frac{dy}{dx} = -\frac{x}{c_1 + c_2 x + c_3 x^2}.$$ 

This latter curve comprises the other two as special cases, and so far as my investigations have yet gone practically covers all homogeneus statistics that I have had to deal with. Something still more general may be conceivable, but I have hitherto found no necessity for it.

To demonstrate its fitness and the importance of these generalised frequency distributions for various problems in physics, economics, and biology, I have devoted the remainder of this paper to the consideration of special cases of actual statistics.

**Part II.—Statistical Examples.**

(21.) Quetelet, who often foreshadowed statistical advances without perceiving the method by which they might be scientifically dealt with, has treated of the subject of limits in Lettre XXII of his "Lettres sur la Théorie des Probabilités" (1846). He seems to have been conscious that certain variations in excess or defect might biologically or physically be impossible, and he accordingly introduces the terms *Limites extraordinaires en plus et en moins* to mark the range of possible variation. He makes no attempt to show how this range may be found from a given set of statistics.

"Lorsqu'on suppose le nombre des observations infini, on peut porter les écarts à des
distances également infinies de la moyenne, et trouver toujours des probabilités qui y correspondent. Cette conception mathématique ne peut évidemment s'accorder avec ce qui est dans la nature. . . . Les limites extraordinaires au delà desquelles se trouvent les monstruosités, me semblent plus difficiles à fixer."

Indeed Quetelet's attempt to fix these limits in the case of the height of human beings at 2·801 and '433 metres is purely empirical, and scientifically worthless.

I propose in this the first section of the practical part of this paper to consider how far the theory we have developed in the first part, enables us to find the range in various groups of physical and biological phenomena.

Example I. The Range of the Barometer.—The following results for the curve of barometric heights are given on p. 352.

\[
\begin{align*}
\alpha &= 171.6 \\
\mu_3 &= 10.14 \\
\mu_0 &= 15.95 \\
\mu_4 &= 326.34.
\end{align*}
\]

We have accordingly:

\[
2\mu_2(3\mu_3^2 - \mu_4) + 3\mu_5^2 = 400.581,
\]

that is, this expression is positive, and we have a limited range.

We have further: \(\beta_1 = 24401, \beta_2 = 317391\).

Hence, determining the constants in the manner described in §14, we have:

\[
\begin{align*}
r &= 30.1382 \\
\epsilon &= 150.7954 \\
b &= 43.61016, \\
m_1 &= 53352 \\
\alpha_1 &= 8.2688 \\
m_2 &= 22.8030 \\
\alpha_2 &= 35.3414.
\end{align*}
\]

Next to find \(d\), giving the distances of the centroid from the origin, or the distance on barometer between mean and maximum, we have by p. 370

\[
d = -8.983.
\]

Thus

\[
\text{Range of barometer above mean} = 9.1671
\]

\[
\text{,, ,, below ,,} = 34.4431.
\]

Now, in the scale upon which our curve is drawn in Plate 10, fig. 6, each centimetre equals \(\frac{1}{10}\) inch, and the mean barometer in Dr. Venn's results equals about 29°931. Thus the maximum possible = 30°85 and the minimum possible = 26°49; the range of the barometer being about 4°36. Now, the highest barometer in Dr. Venn's record = 30°7, and the lowest 28°7; it is clear, therefore, that we reach much nearer in
practice to the upper than to the lower limit of the barometric range. The result here obtained for the barometric range is of course only tentative and approximate. For larger statistics must be dealt with, and for a greater variety of places, we shall then be better able to judge how far the range, as ascertained from Dr. Venn’s statistics, is local, or if general, what modification or correction may be required.

Calculating the value of $y_0$, we find for the curve of barometric heights:

$$y = 21.642 (1 + x/8.2688)^{-3225} (1 - x/35.3414)^{28.8230}.$$  

This curve is traced on Plate 10, fig. 6. It will be seen to be extremely close to the observations.

Although the expression $2\mu_3 (3\mu_3^3 - \mu_4) + 3\mu_3^3$ is not zero, it is interesting to see with what closeness the skew curve which is the limit to a point binomial can be fitted to the barometric observations. This is the curve of Type III. Calculating its constants by aid of § 18, we find

$$y = 22 (1 + x/12.1063)^{22.983} e^{-x^2/271.95},$$  

while $d$, the distance between the maximum ordinate and the centroid-vertical, = 7.864. This gives a maximum possible height of the barometer of 31.22 instead of 30.85, there being of course no lower limit. The curve is shown in Plate 10, fig. 6, and will be seen to give a very close correspondence with the observations. The “skewness” of barometric results as given by the curve with limited range = 0.3983/3.184 = .2821, and as given by the curve of Type III. = 0.7864/3.184 = .2470,—no very great difference.

The areal deviations of the two curves are almost exactly the same, being about 7.1 sq. centims. or percentage error of 4.1. The normal curve is also drawn on the same plate. It diverges widely from the observations, the areal deviation =26 sq. centims. or the percentage error 15.1,—about 3.7 times as great as in the case of either skew probability curve.

Till a wider range of barometric observations have been analysed, it may be wiser not to draw too definite conclusions from the above results, contenting ourselves with the remark that the new skew curve gives far better results than the old normal curve of errors.

---

* I am unaware if Dr. Venn’s results are reduced to sea-level. The lowest recorded barometric height for the British Isles reduced to sea-level is 27".333 (at Ochertyre, Perthshire, January 26, 1884) and the highest (at Roche’s Point, Cork, February 29, 1882) is 30°.83. A statement that the barometer stood at 31°.046 at Gordon Castle, in January, 1820, has hardly sufficient evidence. Supposing Dr. Venn’s statistics to be unreduced Cambridge statistics, the expression theoretically found for the barometric range seems to be on the whole satisfactory. I have at present in hand other series of barometric heights.
Example II. Professor Weldon's Crab Measurements No. 4. The details of these are given in 'Phil. Trans.' vol. 185, p. 96.

We have
\[ \begin{align*}
\alpha &= 999, \\
\mu_3 &= 7.6759, \\
\mu_4 &= 184.3039, \\
\beta_1 &= -0.0267022, \\
\beta_2 &= 3.12807.
\end{align*} \]

In this case
\[ 2\mu_3 (3\mu_3^2 - \mu_4) + 3\mu_3^2 = \mu_2^3 (6 + 3\beta_1 - 2\beta_2) = -\mu_2^3 \times 1.760334, \]
and is accordingly negative. In Example I. of the barometric heights we had
\[ 2\mu_3 (3\mu_3^2 - \mu_4) + 3\mu_3^2 = \mu_2^3 \times 3.8421. \]

Since, in the latter case, this value was sufficiently small to give a good curve of Type III., we may expect the like result in this case. There is, indeed, a slight but sensible skewness even in this the most symmetrical of all Professor Weldon's crab measurements, and the skew curve of Type III. is really a better fit than the normal curve. But clearly since the critical function is negative, we are dealing properly with a case of a curve of Type IV. The ratio of the organs dealt with in No. 4 series of measurements does not give a "limited range" of variation. Proceeding by the method indicated in § 19, we find for the constants
\[ \begin{align*}
\gamma &= 71.624, \\
\delta &= 36.812, \\
\nu &= 25.7616, \\
\alpha &= 21.909, \\
\mu &= 7.8802, \\
\beta &= -2.1407, \\
\delta &= -0.077267, \\
\gamma &= 1.75509. \]

Thus the equation to the curve is:
\[ y = 1.75509 \frac{e^{-25.7616 \tan^{-1}(x/21.909)}}{[1 + x^2/(21.909)^2]^{3.8421}}. \]

To trace the curve, take:
\[ \begin{align*}
x &= 21.909 \tan \theta, \\
y &= 1.75509 \cos^{2\gamma \delta^2} \theta e^{-25.7616}. 
\end{align*} \]

If we take a skew curve of Type III., we find for its equation:
\[ y = 144.22 (1 + x/33.683)^{14.8} e^{-4.41706x}, \]
where, for the centroid
\[ d = 0.226364, \]
and the skewness
\[ \gamma = 0.081704. \]

For the normal curve we have:
\[ y = 143.85 e^{-x^2/(2.77054)^2}. \]

\(^* y_0 \) was calculated by aid of the approximate formula on p. 350.
All three curves are drawn in fig. 4 of Plate 8. It will be seen that they are all very close to the observations. So far as skewness is concerned, curves of Types III. and IV. give practically the same result (0'082 and 0'077); in both cases the skewness is small. The areal deviations are in the three cases respectively: 4'4 sq. centims., 5'9 sq. centims., and 6'7 sq. centims., or we have mean percentage errors in frequency of 4'4, 5'9, and 6'7 nearly; the percentage error for the closest point binomial is 10'5. We thus conclude that even in a case which has been selected as the most typically symmetrical series of measurements out of a very considerable set of careful statistics, the generalised probability curve is one-third as good again as the normal curve, while the special case of that generalised probability curve—which is not the most appropriate to our observations—is itself distinctly better than the normal curve. This result has been confirmed by a considerable application of these generalised curves; in good cases of normal curve fitting, the generalised curves are always sensibly better; in cases where the normal curve is almost useless, as in the case of barometric observations, the new curve, *if of the appropriate type*, will represent with a 4 to 5 per cent. mean accuracy many observations not yet reduced to statistical theory. It is, perhaps, unnecessary to repeat that this mean percentage is much less than the average of what has been allowed to pass muster hitherto in both physical and biological measurements. Professor Edgeworth's view* thus seems untenable; a curve with a comparatively easy theory of its constants has been found which excels the accuracy of the hitherto adopted normal curve. And this for the simple reason that it would pass into the normal curve, if that curve were itself the best fit.

23. *Example III.*—The following statistics of *height* for 25,878 recruits in the United States Army, are given by J. H. Baxter, 'Medical Statistics of the Provost-Marshal-General's Bureau,' vol. 1, Plate 80, 1875.

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* 'Phil. Mag.,' vol. 24, p. 334, 1887.

MDCCCXCV.—A.
I find:

Mean height = 67".2989.
Standard deviation = 2".5848.
Maximum ordinate, 3994.04.

This gives a very close-fitting normal curve.
The data for a generalised curve are

\[
\begin{align*}
\mu_2 &= 6.68122 \\
\beta_1 &= 0.005769 \\
\mu_3 &= -1.31168 \\
\beta_3 &= 3.024801 \\
\mu_4 &= 135.02324
\end{align*}
\]

Thus,

\[2\beta_2 - 3\beta_1 - 6 = 0.032295,
\]

and being positive, we see the curve belongs to Type IV. There is, thus, exactly as in the previous examples of crab measurements, no range of a limited character for these statistics of height.* For a true normal curve, \(\beta_1, \beta_3\) ought to be 0 and 3 respectively; we have therefore a still closer approach (3.025) than in the case of the crabs (3.128) to normality. In this case \(r\) is about 400, and on any reasonable scale, there is no sensible difference between the normal and the generalised curves. The skewness is very slight, = 0.038 about, or about half its value in the case of the crabs.

24. Example IV.—Height of 2192 St. Louis School Girls, aged 8.—The following statistics are given by W. T. Porter, “The Growth of St. Louis Children,” Trans. of Acad. of Sci. of St. Louis,” vol. 6, p. 279, 1894.

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The following are the calculated values of the constants†:

* If, notwithstanding, we take a curve of Type III., we find the range limited on the 'dwarf' side at about '7645'.

† The unit of all these constants = 2 centims., except in the case of the mean height. The standard deviation = 5.55244 centims., which gives a probable deviation of 3.745 centims. The mean
\[
\begin{align*}
\mu_d &= 7.70739, & \text{Mean height} &= 118.271 \text{ centims.}, \\
\mu_s &= 2.38064, & \text{Standard deviation} &= 2.77622, \\
\mu_4 &= 192.17419, & y_0 \text{ for normal curve} &= 314.99, \\
\beta_1 &= .0123784, & \beta_2 &= 3.235045.
\end{align*}
\]

Thus \(2\beta_2 - 3\beta_1 - 6\) is positive, and the curve is again of Type IV.

We have
\[
\begin{align*}
d &= .135606, & \text{Skewness} &= .04885, \\
v &= 4.56967, & m &= 16.4011, \\
r &= 30.8023, & \alpha &= 14.9917, \\
y_0 &= 235.323,
\end{align*}
\]

or, for the equation to the curve:
\[
\begin{align*}
x &= 14.9917 \tan \theta, \\
y &= 235.323 \cos^{32.8023} \theta e^{-1.569674},
\end{align*}
\]

the axis of \(x\) being positive towards dwarfs and the origin 2.2241 on the positive side of the centroid-vertical.

The maximum ordinate = 324.18 and occurs at \(x = -2.0884\).

The curve of Type IV., together with the normal curve, is drawn (Plate 10, fig. 7).

If we attempt to fit a curve of Type III., we find \(p\) about 322.14, and the range limited on the dwarf side at about 99.812 centims. from the mean, or at a height of about 18.5 centims. The largeness of \(p\) causes this curve to coincide with the normal curve to the scale of our diagram. The areal deviations are for the curve of Type IV. and for the normal curve 6.1 and 8.3 centims., giving percentage mean errors of 5.56 and 7.66 in the ordinates respectively. The advantage is again on the side of the generalised curve. It will be seen at once that the normal curve by no means well represents the number of girls of giant height. The theoretical probability that these giants should occur is small, and their actual redundancy over the numbers indicated by the normal curve suggests some peculiarity in this direction; it is fully met by the curve of Type IV. The asymmetry of the curves given by anthropometrical measurements on children has been noted both by Bowditch* and Porter,† but in their published papers, to which I have had access, they do not give their raw material, only the ogive curve arising from Galton's method of percentiles. Unfortunately, theoretical evaluation of the skewness of anthropometric statistics can only be applied or verified when we have raw material, and not integral frequency.
curves, the integral of the frequency in all suggested forms of the frequency curve being not expressible in terms of undetermined constants. Valuable as is the method of percentiles for representing popularly the numerical facts of anthropometry, it is to be regretted that percentile statistics are replacing the raw material in so many publications. The raw material of Professor Weldon's crab-measurements and Bowditch and Porter's child-measurements ought to be preserved and circulated in print, as a means of developing and testing statistical theory.

(25.) Example V. Length-Breadth Index of 900 Bavarian Skulls.—The following statistics are taken from Tables I.-VI., VIII.-X., inclusive, of J. Ranke's 'Beiträge zur physischen Anthropologie der Baiern, München, 1883.' They include all the material, which may be treated as typically "Alt-Baierisch," both male and female skulls.

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<td>37</td>
<td>88</td>
<td>34-5</td>
<td>98</td>
<td>1</td>
</tr>
<tr>
<td>79</td>
<td>55</td>
<td>89</td>
<td>19</td>
<td>99</td>
<td>0</td>
</tr>
</tbody>
</table>

We find, as before,

Position of centroid-vertical, 83'07111,

\[ \sigma = 3'468, \quad y_0 = 103'532 \text{ (for normal curve)}, \]

\[ \mu_2 = 12'027166, \quad \beta_1 = 0078995, \]

\[ \mu_3 = 3'707179, \quad \beta_2 = 3'649553, \]

\[ \mu_4 = 52'91696, \quad r = 12'42734, \]

\[ d = 111388, \quad \text{Skewness} = 0321186, \]

\[ m = 7'21367, \quad \nu = 853'771, \quad a = 11'69583, \quad y_0 = 107'4706. \]

Thus we see that the curve is again of Type IV. This result seems of considerable significance, but it requires, of course, wider examination of cases than I have yet been able to make. But, so far as I have gone, in both anthropometric and biological statistics, whether relative or absolute measurements of organs, the frequency curves all deviate from the normal curve—however slight the deviation—in the direction of Type IV. That is to say, the distribution of chances upon which the frequency of variation of an organ depends, appears to resemble the drawing of a

* Indices such as 73·5 have been divided between 73 and 74 groups.
limited amount from a limited mixture. So far as this goes, it is evidence against
the usual hypothesis that in biological matters the chances of deviations on either
side of the mean are equal, and the "contributory causes" independent and
indefinitely great in number. Thus we appear in biological statistics to be dealing
with a chance system corresponding, not to a binomial, but to a hypergeometrical
series, such as that discussed in § 11.

If it be remarked that Type IV. dismisses at once the problem of range from
biological investigations, we must notice that, while this is theoretically correct so
long as we are dealing with the continuous curve by which we replace the hyper-
geometrical series, it is not true the moment we fall back from the curve on the point
series (see p. 361). If the \( r \) of that page (or the \( qn \)) be an integer, the series is limited
in range. It seems very possible that discreteness, rather than continuity, is charac-
teristic of the ultimate elements of variation; in other words, if we replaced the curve
by a discrete series of points, we should find a limited range. It is the analytical
transition from this series to a closely fitting curve which replaces the limited by an
unlimited range. Exactly the same transition occurs when we pass from the sym-
metrical point binomial to the normal curve. Thus, while Type I. marks an absolutely
limited range, the occurrence of Type IV. does not necessarily mean that the range
is actually unlimited.*

For the equation to the curve we have
\[
x = 11.69583 \tan \theta,
\]
\[
y = 107.4706 \cos^{11/1273} \theta e^{-33377\theta},
\]
the origin being at a distance \( 803515 \) on the positive side of the centroid vertical.

The normal curve as well as the curve of Type IV. are shown (Plate 11, fig. 8). The
result in both cases is quite good for this type of statistics—\( i.e. \), the skulls came from
eight different districts and include 100 female skulls. With the planimeter the areal
deviation in both cases = 6.8 square centims., giving in either case an average per-
centage error of 7.56. That the generalised curve does not in this case give a
decidedly better result than the normal curve I attribute to the heterogeneity of the
material. It clearly accounts better for the extreme dolichocephalic and brachy-
cephalic skulls than the normal curve. The same 900 skulls have been fitted with a
normal curve by Stieda,† but neither the constants of his normal distribution nor

* I reserve for the present the fitting of hypergeometrical point series to statistical results. The
discussion is related to curves of Type IV., as the fitting of point binomials to curves of Type III. It
will, I think, throw considerable light on the nature of chance in the field of biological variation,
especially with regard to limitation of the material to be drawn upon, to which I referred above, and
which, I believe, finds confirmation in skull statistics.

† "Über die Anwendung der Wahrscheinlichkeitsrechnung in der anthropologischen Statistik,"
his plotting of Ranke's observations agree with mine. He has added together under 83, for example, all indices from 83 to 83.9. Thus, for the indices 81, 82, 83, 84 he gives the frequencies 106, 92, 111, 99, while I find 82, 116, 98, 107, a very sensible difference.* Stieda's method can introduce very sensible errors. In this particular case it transfers the maximum frequency of observation from 82 to 84.

The last four examples have dealt with cases where the statistician has hitherto been content to assume symmetry. They have been given to indicate (i.) an apparently uniform trend in biological statistics of variation, and (ii.) the improved fitting of theory to practice which arises from using the generalised curve. I now pass to cases of obvious skewness, where the statistician has hitherto had no satisfactory theory.

(26.) Example VI. Distribution of 8689 Cases of Enteric Fever Received into the Metropolitan Asylums Board Fever Hospitals, 1871-93.

<table>
<thead>
<tr>
<th>Age</th>
<th>Number of cases</th>
<th>Age</th>
<th>Number of cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under 5</td>
<td>266</td>
<td>35-40</td>
<td>299</td>
</tr>
<tr>
<td>5-10</td>
<td>1143</td>
<td>40-45</td>
<td>163</td>
</tr>
<tr>
<td>10-15</td>
<td>2019</td>
<td>45-50</td>
<td>98</td>
</tr>
<tr>
<td>15-20</td>
<td>1213</td>
<td>50-55</td>
<td>40</td>
</tr>
<tr>
<td>20-25</td>
<td>1319</td>
<td>55-60</td>
<td>14</td>
</tr>
<tr>
<td>25-30</td>
<td>857</td>
<td>Above 60</td>
<td>13</td>
</tr>
<tr>
<td>30-35</td>
<td>563</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

I considered that the 13 cases "above 60" might be distributed as follows: 60-65, 8; 65-70, 4; 70-75, 1.

Taking five years as the unit I found

\[ \mu_2 = 4.070554, \quad \mu_3 = 7.598196, \quad \mu_4 = 69.379605. \]

The centroid-vertical is at 18.9691 years, i.e., 29382 unit from 15-20.

Thus \(2\mu_2 (3\mu_3^2 - \mu_1) + 3\mu_3^2 = 13.05102,\) or the curve is of Type I. Since, however, \(3\beta_1 - 2\beta_2 + 6 = .1935\) is small, a curve of Type III. will also be a good fit.

We have for the other constants

\[ r = 72.28642, \quad d = .98643, \]
\[ e = 259.78912, \quad \text{Skewness} = .488922, \]
\[ b = 77.28312, \]
\[ m_1 = 2.79291, \quad m_2 = 67.49351, \]
\[ a_1 = 3.07801, \quad a_2 = 74.20551, \]
\[ y_0 = 1890.83. \]

*I class as 83 all from 82.6 to 83.4, dividing 82.5 between 82 and 83 evenly, and 83.5 between 83 and 84 evenly. Thus in the Table above certain frequencies will be found with such values as 12.5 or 71.5 skulls.
Thus we have for the curve of Type I.

\[ y = 1890.83 \left(1 + \frac{x}{3.07801}\right)^{2.79391} \left(1 - \frac{x}{74.2051}\right)^{67.46561}, \]

where the centroid is 98643 unit from axis of \( y \).

The curve of Type III. is

\[ y = 1894.57 \left(1 + \frac{x}{3.428094}\right)^{3.673042} e^{-1.071453x}. \]

The centroid is in this case 933313 unit on the positive side of the origin and the skewness = 462594.

It will be noticed that the curve of Type I. extends 2706 unit or 1.353 years, and the curve of Type III. 5676 unit or 2.838 years before birth. In both cases the chances of an “antenatal” death from enteric fever are very, very small. Curve of Type I. is in this respect better than the curve of Type III. The latter curve gives no maximum limit, the former a limit of about 77 units or 385 years. In both cases, however, the chances of a case of enteric fever with the subject over 100 years are vanishingly small. These statistics of enteric fever thus set a maximum limit to the duration of life, but it is a limit so high as to have little suggestiveness.

In order to see what is the nature of the difference made, when we suppose the liability to enteric fever to commence with birth, I will treat these statistics as a case falling under § 16.

If then \( \mu', \mu_2', \) and \( \mu_3' \) be the first three moments about the vertical through 0 years we have

\[ \mu_1' = 379382, \quad \mu_2' = 1846362, \]
\[ \mu_3' = 10653175, \]
\[ \chi_2' = 1.323213, \quad \chi_3' = 1.549399, \]
\[ \alpha_1 = 0.030435, \quad \alpha_2 = 321856, \]
\[ n_1 = 2.14296, \quad n_3 = 28.71414, \]
\[ b = 40.1206, \quad y_0 = 1873.39, \]
\[ a_1 = 2.78629, \quad a_3 = 37.33431. \]

whence we have for the curve

\[ y = 1873.39 \left(1 + \frac{x}{2.78629}\right)^{2.14296} \left(1 - \frac{x}{37.33431}\right)^{28.71414}. \]

Here the duration of life is 200 years about, and the maximum incidence of the disease is at 13.93 years.

Lastly for the normal curve, we have the constants \( \sigma = 2.01756 \) units = 10.0878 years and \( y_0 = 1718.12. \)

All the above four curves are drawn, Plate 12, fig. 9.
We see at once that the normal curve is perfectly incapable of expressing statistical results like these. It gives an average error in the ordinate of 25.8 per cent. and no less than 260 antenatal deaths!

For the remaining three curves we have the following results:—

<table>
<thead>
<tr>
<th>Curve of Type I. (closest fit)</th>
<th>Percentage error in ordinate</th>
<th>Antenatal cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot; &quot; (starting at birth)</td>
<td>5.75</td>
<td>3</td>
</tr>
<tr>
<td>Curve of Type III.</td>
<td>7.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5.38</td>
<td>9</td>
</tr>
</tbody>
</table>

The percentage errors here are well within those usually passed by statisticians. If they are slightly larger than what we have found in previous cases the source of the error is not far to seek. We have combined both male and female cases, but the distributions of enteric fever for both sexes are not the same. The fever curves for either sex differ in some cases markedly, although less for enteric fever than for diphtheria, for example. We have thus, in reality, a compound curve. I have found for about 700 male cases only a percentage error of about 5.*

Another point needing notice is the question of antenatal cases, which may at first strike the reader as absurd. The closest fitting curve of Type I. runs, as we have seen, 1.35 years about before birth, and gives three antenatal cases. Three antenatal cases (or, indeed, 9 in the case of the curve of Type III.) is a very small percentage of 8689 cases, and not of importance from the statistician's standpoint. But the fact that a curve starting before birth gives a better fit than one starting at birth, is significant, and there is every probability that a curve starting from about 1.75 year would give a still less percentage error than one from 1.35 year or from birth.†

In dealing with mortality curves for infancy I have found it impossible to get good fitting theoretical curves, without carrying these curves backward to a limit of something less than a year. The “theoretical” statistics thus obtained of antenatal deaths seem to be fairly well in accordance with the actual statistics of maternity charities. In vital statistics therefore we must be prepared in most diseases for small percentages of antenatal cases and antenatal deaths, and it is just possible that theory in this matter will be able to indicate lines of profitable inquiry to the medical statistician.

(27.) Example VII.—As an example of the method of Section 15, I take the following statistics of guessing a tint. Nine mixtures of black and white were taken,

---

* I propose on another occasion to deal with the age distribution of fever cases. My object at present is only to give typical illustrations of the method of calculating skew curves.
† In fact the case of a pregnant woman with enteric fever is to be considered as a case also of antenatal enteric fever.
so as to get a series of tints in arithmetical progression 1, 2, 3, 4, 5, 6, 7, 8, and 9. These tints were then placed in non-consecutive order, and 231 persons asked to guess a tint by affixed letters lying between 1 and 9. The results were as follows:

<table>
<thead>
<tr>
<th>Tint</th>
<th>Frequency of guess</th>
<th>Tint</th>
<th>Frequency of guess</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>6</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Now, obviously, the number of tints and the number of persons guessing were far too limited to draw any definite conclusions as to the distribution of tint guesses. I propose here merely to use these statistics to illustrate the calculation of a skew frequency curve with a given limited range. I do not wish to propound any theory of tint guessing, nor to assert that these guesses actually distribute themselves according to the curves dealt with in this paper.

Calculating the moments about the centroid in the usual manner, we have

\[
\begin{align*}
\mu_2 &= 2.1417 \\
\mu_3 &= -3.70067 \\
\mu_4 &= 19.6255
\end{align*}
\]

Centroid lies at a distance of 5.876624 units from the tint 1.

We easily find \(2\mu_2 (3\mu_2^2 - \mu_4) + 3\mu_2^2 = 15.96335\), or the observations fall into a curve of Type I, that is to say, have a limited range.

We obtain

\[
\begin{align*}
\beta_1 &= 1.39407, & \beta_2 &= 4.27862, \\
\gamma &= 6.95847, & \epsilon &= 6.443186.
\end{align*}
\]

hence the range

\[b = 11.31768.\]

Further

\[
\begin{align*}
m_1 &= 4.858705, & m_2 &= 0.099765, \\
\alpha_1 &= 11.68997, & \alpha_2 &= 2.2769, \\
d &= 1.561012, & \text{Skewness} &= 1.06666.
\end{align*}
\]

Thus the range of the theoretical curve runs from a point 4.15233 units before tint 1, and concludes at a point 7.34674 unit before tint 9. The curve is, however,

* I hope later to deal with the subject of tint guesses falling within a limited range, as my material increases in bulk. I would only note here, that the geometrical mean frequency curve does not seem to give results according well with experiment.

MDCCCXCIV. — A.
practically insensible before tint 1. Considering the roughness of the experimental method, the obtaining an actual range of about 11 instead of 8, and its covering very nearly the range of 8 must be held to be fairly encouraging for the method. I shall accordingly calculate the constants of the curve on the assumption that the range lies between Tints 1 and 9, using the method of § 15.

We find

\[ \mu_1' = 2.623376, \quad \mu_2' = 9.023803, \]
\[ \gamma_1 = 327922, \quad \gamma_2 = 429971. \]

Whence

\[ m_2 = 2.75412, \quad m_1 = .81372, \]
\[ a_2 = 6.144435, \quad a_1 = 1.855565, \]

and

\[ y_0 = 59.5996. \]

Thus we may take for the curve

\[ y = 59.6 \left( 1 + \frac{x}{.6144435} \right)^2 \left( 1 - \frac{x}{1.855565} \right)^{.83172}. \]

The curve is figured, Plate 11, fig. 10, with the first "smooth" of the observations. It will be seen to give the general character of the distribution, but much more elaborate experiments would be required before any statement could be made as to whether frequency of tint guesses really does follow a curve with limited range of Type I. On the same plate the frequency of 128 guesses distributed over 18 tints is given, the approximation to a curve of Type I is fairly close considering the paucity of guesses.

(28.) Example VIII.—The question may be raised, how are we to discriminate between a true curve of skew type and a compound curve, supposing we have no reason to suspect our statistics \textit{a priori} of mixture. I have at present been unable to find any general condition among the moments, which would be impossible for a skew curve and possible for a compound, and so indicate compoundedness. I do not, however, despair of one being found. It is a fact, possibly of some significance, that the best fitting skew curve to several compound curves that I have tested is a curve of Type I, and not that of Type IV. which appears to be the more usual type in biological statistics. Taking, as an example, the statistics for the "foreheads" of Naples crabs due to Professor Weldon, and resolved into their components in my memoir, 'Phil. Trans.' A, vol. 185, p. 85, \textit{et seq.}, I find for the best fitting skew curve the equation

\[ y = 83.2526 \left( 1 + \frac{x}{46.9296} \right)^{14.7364} \left( 1 - \frac{x}{11.2125} \right)^{1.0640}, \]

where the origin is at 1.4274 horizontal units from the centroid-vertical in the
positive sense of the horizontal scale. If, now, we place this skew curve and the compound curve of Plate 1, 'Phil. Trans,' vol. 185, on top of the observations (see Plate 13, fig. 11), we see at once how much better is the fit of the compound curve. The skew curve gives a mean percentage error in the ordinates of 10.4, the compound curve of only 7.4. The determination of the best skew curve, when the compound curve is known, is easy, for all its details are already practically calculated.

A criterion of whether a compound or skew curve is to be sought for ab initio, would be, however, of great value.

(29.) Example IX.—A more markedly skew curve than any we have yet dealt with is that giving the frequency of divorce with duration of marriage. I take my statistics from a paper by Dr. W. F. Willcox, entitled "The Divorce Problem, a Study in Statistics" ('Studies in History, Economics, and Public Law,' Columbia College, vol. 1, p. 25). They are as follows:

<table>
<thead>
<tr>
<th>Duration of marriage in years</th>
<th>Divorces (1882–6).</th>
<th>Duration of marriage in years</th>
<th>Divorces (1882–6).</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5314</td>
<td>12</td>
<td>4089</td>
</tr>
<tr>
<td>2</td>
<td>7483</td>
<td>13</td>
<td>3563</td>
</tr>
<tr>
<td>3</td>
<td>9426</td>
<td>14</td>
<td>3144</td>
</tr>
<tr>
<td>4</td>
<td>9671</td>
<td>15</td>
<td>2931</td>
</tr>
<tr>
<td>5</td>
<td>9014</td>
<td>16</td>
<td>2721</td>
</tr>
<tr>
<td>6</td>
<td>8274</td>
<td>17</td>
<td>2217</td>
</tr>
<tr>
<td>7</td>
<td>7021</td>
<td>18</td>
<td>1877</td>
</tr>
<tr>
<td>8</td>
<td>6063</td>
<td>19</td>
<td>1577</td>
</tr>
<tr>
<td>9</td>
<td>5305</td>
<td>20</td>
<td>1459</td>
</tr>
<tr>
<td>10</td>
<td>5002</td>
<td>21 and over</td>
<td>9401</td>
</tr>
<tr>
<td>11</td>
<td>4884</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total number of divorces granted, 109,966.

Now these statistics suffer from a defect common to many of the class—the want of careful enumeration of the frequencies near the beginning and end of the series. It cannot be too often insisted upon that careful details of the frequencies in the start and finish of the distribution are requisite if we are to fit skew distributions with their appropriate skew curves. How, in this case for example, are we to distribute the 9401 divorces which occur after 21 years of married life? How, on the other hand, does the curve start? It is impossible to place 5314 divorces at the mean—6 months—of the one year duration. It is obvious that the applications for divorce will be far more numerous in the last half-year than the first half-year of matrimony. The very time required to institute legal proceedings and get a divorce granted must ensure this if nothing else did. Yet these two tails of 5314 and 9401, of which the accurate distributions are not given, are between $\frac{1}{2}$ and $\frac{1}{3}$ of the total number of divorces, and until we know how they are exactly distributed, we cannot hope for the very exact fitting of a theoretical curve.

3 E 2
In order to make the best of the "tails" under the circumstances, their moments were calculated on two hypotheses, (i.) that they were triangles, (ii.) that they were logarithmic curves, and the mean of these extreme results taken.

I found

\[ \mu_2 = 60.7376, \quad \mu_3 = 809.15, \]
\[ \gamma = 1.50127, \quad \rho = 3.6891. \]

Distance of centroid from start of curve = 9.1183,

maximum \, Distance of \, centroid \, from \, start \, of \, curve \, = \, 2.4373,

\[ y_0 = \text{maximum frequency} = 8882.45. \]

Here the curve is assumed, owing to the obviously long tail to the right and the abrupt start to the left, to be of Type III. Its equation is accordingly

\[ y = 8882.45 \left(1 + \frac{x}{2.4373}\right)^{3.6891} e^{-1.50127x}, \quad \text{Skewness} = 8.547. \]

The curve is figured, Plate 11, fig. 12, and will be seen to rise abruptly at about '47 of a year's duration. It may be doubted whether legal proceedings even in America are so rapid that a divorce suit can be complete within six months of marriage. The curve gives fairly well the general form of the frequency statistics. Could the moments have been determined with greater accuracy, most probably a better fit would have resulted. As it is the mean percentage error is above 6.

(30.) Example X.—A still more extreme case may be selected from the field of economics. I take the following numbers from the 1887 Presidential Address of Mr. Goschen to the Royal Statistical Society ('Journal,' vol. 50, Appendix II. pp. 610–2). I have grouped together both houses and shops, because the details of the two are not in Mr. Goschen's returns separated for values under £20.

### Valuation of House Property, England and Wales, years 1885 to 1886.

| Valuation of House Property, England and Wales, years 1885 to 1886. |
|-------------------|-------------------|-------------------|
| Under £10         | 3,174,806         | £80 to £100       |
| £10 to £20        | 1,450,781         | 100 " 150        |
| 20 " 30           | 441,595           | 150 " 300        |
| 30 " 40           | 259,756           | 300 " 500        |
| 40 " 50           | 150,968           | 500 " 1,000      |
| 50 " 60           | 90,432            | 1,000 " 1,500    |
| 60 " 80           | 104,128           | 1,500 " 2,000    |

<table>
<thead>
<tr>
<th>Number of houses.</th>
<th>Number of houses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>47,326</td>
<td>58,871</td>
</tr>
<tr>
<td>37,988</td>
<td>8,781</td>
</tr>
<tr>
<td>3,002</td>
<td>1,036</td>
</tr>
</tbody>
</table>

Here clearly the curve starts with the maximum frequency, and further to any
scale to which the curve can be drawn, it tails away indefinitely to the right. This justifies us in the assumption that the curve will be fairly approximated to by a form of type

\[ y = y_0 x^p e^{-mx}, \]

where \( p \) would turn out to be a negative quantity lying between 0 and 1. But the details given us of the start and finish of the curve are far too scanty to allow us to proceed by moments. In the first place, to measure an element of area of the frequency curve by an element of value into its mid-ordinate is perfectly legitimate at such a point as B; it fails entirely, however, at such a point as A, which includes the part of the curve which is asymptotic to the ordinate of maximum frequency. The area at such a point is much greater than the element into the mid-ordinate, and the calculation of moments on the assumption that 3,174,806 houses may be concentrated at £5, is purely idle. The ordinate obtained from the area in this manner may often differ 30 per cent. from the true ordinate, and yet about three-fifths of the total number of houses fall into this first group.

Further treating the area as ordinate into element of value is also true only if the element of value be small. For "elements" such as £150, £200, or even £500, which are all that are given in the tail of these statistics, it is perfectly idle to concentrate the area at the mid-ordinate. The centroid of a piece of tail such as the accompanying figure suggests lies far to the left of the mid-ordinate. In other words, to attack the problem by the method of moments, we require to have the "tail" as carefully recorded as the body of statistics. Unfortunately the practical collectors of statistics often neglect this first need of theoretical investigation, and proceed by a method of "lumping together" at the extremes of their statistical series.

Still three further points in regard to the present series of statistics. First, they are
very unlikely to be homogeneous. Houses with an annual valuation of over £300 hardly fall under the same series of causes as the bulk of houses in the kingdom which fall under £100. Secondly, when we are told that 3,174,806 houses are valued under £10, it can hardly mean that any houses are valued at 0, certainly not the maximum number. Hence our frequency curve in theory must not be expected to rise from zero, but from some point between 0 and £10, which corresponds to the customary minimum at which a cottage can be rented.

Lastly, there is one special cause at work tending to upset, about the value of £20, the general distribution due to a great variety of small causes. This is the value at which taxation commences, and we should expect a larger proportion of houses to be built just under the taxable value than is given by a chance distribution.

Notwithstanding the many disadvantages of these results, I determined to obtain if possible a skew curve approximating to the main portion of the distribution. I took £10 as my unit of value and 1000 houses as my unit of frequency. I started with the ordinary method of moments, concentrating each area at its centroid as given by the total valuation of the group, also recorded by Mr. Goschen, and found a curve of the type

$$ y = y_0 x^p e^{-\gamma x}, $$

with

$$ p = -0.65448, \quad \gamma = 2.003. $$

This was so far satisfactory that it showed even by this rough method that $p$ was negative, and between 0 and 1. Thus the theoretical curve gave an infinite ordinate, but finite area at its start.

A laborious method of trial and error was then adopted, and by varying $p$ and $\gamma$ slightly, as well as $y_0$ and the origin of the curve, I sought to improve the fit given by the rough method (in this case) of moments. The fundamental consideration was to keep the total areas under £100 value as nearly as possible the same in the theoretical curve and the statistics. This portion of the curve I treated as practically referring to homogeneous material. Ultimately I found the following curve:

$$ y = 1388.32 x^{-0.0077} e^{-3.06712x}, $$

with the origin as '45 unit from zero. Thus the minimum annual valuation was £4 10s., or, to a weekly valuation, of 1s. 7½d. This would connote probably a weekly rental of 1s. 8d. to 2s. The total area of this theoretical curve was 5795 in thousands of houses; of these 5729 had a valuation under £100 and 66 over £100; the corresponding numbers for the statistics themselves are 5720 and 110. The additional 44 over £100 I assume to be due to the heterogeneity of the statistics—high values corresponding to blocks of chambers, large hotels and other buildings hardly falling into the same category as the small house under £100 in value. Unfortunately the "tail" of the statistics is so defectively recorded that there is no hope of reaching a separate distribution for this high class property.
Returning now to the curve and statistics, we have the following comparative results:

<table>
<thead>
<tr>
<th>Value</th>
<th>Number of 1000's of houses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory</td>
</tr>
<tr>
<td>£</td>
<td></td>
</tr>
<tr>
<td>Under 10</td>
<td>3580</td>
</tr>
<tr>
<td>10-20</td>
<td>1045</td>
</tr>
<tr>
<td>20-30</td>
<td>452</td>
</tr>
<tr>
<td>30-40</td>
<td>253</td>
</tr>
<tr>
<td>40-50</td>
<td>133</td>
</tr>
<tr>
<td>50-60</td>
<td>97</td>
</tr>
<tr>
<td>60-80</td>
<td>102</td>
</tr>
<tr>
<td>80-100</td>
<td>46</td>
</tr>
<tr>
<td>Above 100</td>
<td>66</td>
</tr>
</tbody>
</table>

The general accordance here is very marked, the chief divergences being accounted for by the special causes to which we have referred above, i.e. (i) the crowding of houses just below the limit of taxation, and (ii) the divergent character of the causes at work determining the frequency of low and high class house property.

The results are depicted, Plate 14, fig. 13.

It will be observed that so far as the observations can be plotted to the theoretical curve, it leaves little to be desired. The histogram* shows, however, the amount of deviation at the extremes of the curve.

(31.) Example XI.—Frequency curves of the type considered in Example X. are so common that it is needful to make a few further remarks with regard to them, and illustrate them by further examples. Such curves occur in many economical instances (income tax, house valuation, probate duty), in vital statistics (infantile mortality), and not uncommonly in botanical statistics of the frequency of variations in the petals or other characteristics of flowers.

As we have noted, the method of moments developed in this memoir cannot be directly applied, or only applied to obtain a first approximation to the constants required. This first approximation, however, will often assist us to obtain with quite sufficient accuracy the value of the moments of portions of the area, especially if the position of the initial or asymptotic ordinate is known.

For example, consider the curve of limited range:

\[ y = y_0 x^{-p} (b - x)^{\alpha} \]

where \( p \) lies between 0 and 1. Then if \( a \) be its area, \( a \mu''_a \) = the \( s^{th} \) moment about the asymptotic ordinate of the area up to \( x \):

* Introduced by the writer in his lectures on statistics as a term for a common form of graphical representation, i.e., by columns marking as areas the frequency corresponding to the range of their base.
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\[
u''(x) = \int_0^\infty y_0 x^{r-1} (b - x)^{\gamma} \, dx
\]

\[
= y_0 b^x \left\{ \frac{1}{1 + s - \beta} - \frac{nx}{b (2 + s - \beta)} + \frac{n \cdot \beta - 1}{1.2 (3 + s - \beta)} \left( \frac{x}{b} \right)^2 \right\} x^{1 + s - \beta}.
\]

Hence, if the range \( b \) be large and \( x \) be small, this series converges very rapidly, and we may often take with sufficient approximation even only its first term. Thus

\[
\begin{align*}
\mu''_1 &= x \frac{1 - \beta}{2 - \beta} \\
\mu''_2 &= x^2 \frac{1 - \beta}{3 - \beta} \\
\mu''_3 &= x^3 \frac{1 - \beta}{4 - \beta} \\
\alpha &= \frac{y_0 b^x}{1 - \beta} \cdot x^1 \cdot \gamma
\end{align*}
\]

Now \( \alpha \) is given by the statistics, and we note that if \( \beta \) has been determined to a first approximation by the method of moments, we can now improve the values of the moments of the areas near the asymptotic ordinate by the use of the above expressions.

For example, if \( \beta = .5 \) as a first approximation, we have

\[
\mu''_1 = \frac{1}{3} x, \quad \mu''_2 = \frac{1}{5} x^2, \quad \mu''_3 = \frac{1}{7} x^3.
\]

Concentration along the mid-ordinate in the usual manner would have given us

\[
\mu''_1 = \frac{1}{4} x, \quad \mu''_2 = \frac{1}{4} x^2, \quad \mu''_3 = \frac{1}{5} x^3,
\]

and as the area up to a short distance from the asymptotic ordinate is generally a considerable proportion of the total area, the above values very considerably modify the calculated moments.

In the case of the curve

\[
y = y_0 x^{-\gamma e^{-x}}
\]

we have the result

\[
\alpha\mu''_1 = y_0 x^{r + 1 - \gamma} \left\{ \frac{1}{1 + s - \beta} - \frac{\gamma x}{2 + s - \beta} + \frac{\gamma^2 x^2}{1.2 (3 + s - \beta)} \right\}.
\]

Hence, as before, if \( \gamma \) and \( x \) be small,
\[ \mu'' = \frac{1 - p}{1 + s - p} \approx x^2, \text{ approximately.} \]

Results such as the above enable us to approximate fairly rapidly to the constants of a frequency curve.

As a special example, I take the following. In 1887, Herr H. de Vries transferred several plants of Ranunculus bulbosus to his flower garden, and counted the petals of 222 of their flowers in the following year. He found (Berichte der deutschen botanischen Gesellschaft, Jahrg. 12, pp. 203-4, 1894):

<table>
<thead>
<tr>
<th>Petals</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>133</td>
<td>55</td>
<td>23</td>
<td>7</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Now the series here proceeds by discrete units, and corresponds probably to a hypergeometrical series, but remembering how closely the results of tossing ten coins can be represented by a normal frequency curve, I was not without hope that the areas of a skew frequency curve would give results close to these numbers. The buttercups start with 5 petals and run to 10; I therefore took my origin at 4.5 and determined the constants to a second approximation in the manner above indicated. There resulted,

\[ y = 211225x^{-322} (7.3253 - x)^{3.142}, \]

a curve of Type I., with limited range, the asymptotic ordinate being at 4.5 petals, or practically a distribution ranging from 5 to 11 petals.

Calculating the areas, there results,

<table>
<thead>
<tr>
<th>Petals</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>Theory</td>
<td>136.9</td>
<td>48.5</td>
<td>22.6</td>
<td>9.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Observation</td>
<td>133</td>
<td>55</td>
<td>23</td>
<td>7</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The agreement here is very satisfactory considering the comparative paucity of the observations.† The results are exhibited by curve and histogram, Plate 15, fig. 14; the two points on the "observation curve" corresponding to five and six petals are deduced from the areas given by the statistics by the same percentage reduction as

*Another very serviceable formula is due to Schlämilch. It gives the area of the "tail" of \( y = y_0 x^{-\frac{p-1}{2}} \) from \( x = a \) to \( x = \infty \) in a rapidly converging series, i.e.,

\[ \text{area} = \frac{y_0 a^{-\frac{p}{2}}}{\frac{1}{\gamma}} \left\{ 1 - \frac{p}{\gamma x + 1} + \frac{p^3}{(\gamma x + 1)(\gamma x + 2)} - \frac{p(p^2 + 1)}{(\gamma x + 1)(\gamma x + 2)(\gamma x + 3)} + \text{etc.} \right\}. \]

† 2048 tosses of 10 shillings at a time gave a mean 3 per cent. deviation between theory and experiment, 100 tosses gave about 9 per cent. The above series corresponds to about 7.2 per cent., and thus is quite within the range of accuracy of coin-tossing experiments.

MDCCCXCV. — A.
converts the theoretical areas into the ordinates of the theoretical curve. For other petals, ordinates and areas practically coincide in value.

(32.) Example XII.—Another example of a similar kind may be taken from Herr de Vries’ memoir (loc. cit., p. 202). He cultivated under the name of perumbellatum a race of Trifolium repens, in which the axis is very frequently prolonged beyond the head of the flower, and bears one to ten blossoms. In the summer of 1892 he had a bed of such clover, produce of a single plant, and in July counted the extent of this variation on 630 flowers. In 325 cases the axis, according to de Vries, had not grown through the head of the flower, in 83 cases it had grown through and bore one blossom, in 66 cases two blossoms, and so on. The complete statistics are as follows:—

<table>
<thead>
<tr>
<th>High blossoms</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>325</td>
<td>83</td>
<td>66</td>
<td>51</td>
<td>36</td>
<td>36</td>
<td>18</td>
<td>7</td>
<td>6</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Taking moments in the manner of the earlier part of this memoir, I found as a first approximation to the frequency curve:

\[ y = 4.52842 x^{-0.43317} (10.69114 - x)^{1.47797}, \]

with the origin at 4.7813 to left of maximum ordinate. This first approximation seemed to justify three things: (i.) starting at 5 to the left of the maximum ordinate; (ii.) assuming a range, 11, which just covered the whole series of observations, i.e., from 5 to 10.5; and (iii.) that the moments of the areas might be found from a value of \( p \) not far from 5.

A second approximation was then made, and taking moments round the asymptotic ordinate, I found:

\[ \mu'_1 = 1.8660, \quad \mu'_2 = 7.77028, \]

whence, in the manner of §16, we have:

\[ \chi_1 = 1.698182, \quad \chi_2 = 3.781526, \]

and ultimately:

\[ m_1 = -4.93118, \quad m_2 = 1.47797, \]

and

\[ y_0 = 4.65148. \]

The equation to the frequency curve is therefore:

\[ y = 4.65148 x^{-0.43318} (11 - x)^{1.47797}. \]

The value found for \( p \), i.e., 4.93, justifies our calculation of the moments on the assumption that it was 5.
Placing statistics and theory side by side, we have:

<table>
<thead>
<tr>
<th>Teeth.</th>
<th>Cases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>123</td>
</tr>
<tr>
<td>4</td>
<td>372</td>
</tr>
<tr>
<td>5</td>
<td>349</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>

The centroid-vertical here lies \( 313661 \) of a tooth beyond 4, \( i.e. \), at \( 4\cdot313661 \) teeth. The following are the moments about centroid-vertical:

\[ 3 F 2 \]
\[ \mu_2 = 0.910906, \quad \mu_3 = 0.233908, \quad \mu_4 = 2.625896 \]

where the unit = 1 tooth.

For the normal curve these give

- Standard deviation = 0.9544,
- Maximum ordinate = 382.5.

For the skew curve we have

\[ \beta_1 = 0.072222, \quad \beta_2 = 3.164684. \]

Hence

\[ 2\beta_2 - 3\beta_1 - 6 = 1.22702, \]

or, we have a curve of Type IV. The values of \( \beta_1 \) and \( \beta_2 \), however, show that it will not differ very widely from the normal type.

Proceeding to determine the other constants we find

\[ \begin{align*}
\nu &= 111.398, \\
\nu &= -109.047 \quad (\nu \text{ is negative since } \mu_3 \text{ is positive}), \\
\alpha &= 7.16613, \\
\beta &= 56.699.
\end{align*} \]

Distance of origin from centroid-vertical = 7.0149,

\[ \log y_0 = 18.4431056. \]

Thus

\[ y = y_0 \cos^{129.309} e^{109.9470}, \]

\[ x = 7.16613 \tan \theta \]

give the form of the curve. This curve, the normal curve, and the observations are drawn, Plate 13, fig. 16. A comparison of the observations and the normal curve shows an amount of skewness in the tails of the former, which would be very improbable if the normal curve really expresses the distribution. The skew curve really accounts for this divergence and is a sensibly better fit. The mean percentage errors in the ordinates are for the two cases 8.67 and 3.88. The skew curve is thus an excellent fit.

The discontinuity in these teeth probably corresponds to a hypergeometrical polygon, of which the skew curve is a limiting form.

(34.) Example XIV.—Another extremely interesting illustration of skew variation will be found in the statistics of pauperism for England and Wales, to which my attention was drawn by Mr. G. U. Yule, who had plotted the statistics from the raw material provided in Appendix I. of Mr. Charles Booth’s ‘Aged Poor; Condition’.

In Plate 14, fig. 17, we have 632 unions distributed over a range of pauperism varying from 100 to 850 per 10,000 of the population for the year 1891. The observations
are at once seen to give a markedly skew distribution. Taking 50 paupers as unit of variation, we find

\[ \mu_2 = 6.31889, \quad \beta_2 = 3.060017, \]
\[ \mu_3 = 6.62465, \quad \beta_1 = 3.73942. \]

Hence

\[ 3\beta_1 - 2\beta_2 + 6 = 4.01791, \]

or the curve is of Type I.

The other constants were found to be

\[ r = 28.165013, \]
\[ \epsilon = 148.0886, \]
\[ m_1 = 20.169714, \quad \alpha_1 = 24.2203 \]
\[ m_2 = 5.995305, \quad \alpha_2 = 7.199312 \]
\[ y_0 = 99.9065. \]

Range = 31.4196.
Maximum = 6043.4 to left of centroid vertical.
Skewness = 24.

The equation to the curve is thus

\[ y = 99.9065 \left(1 + \frac{x}{24.2203}\right)^{20.1671} \left(1 - \frac{x}{7.1993}\right)^{20.1671}. \]

For the normal curve,

\[ \text{Standard deviation} = 2.514, \]
\[ \text{Maximum ordinate} = 100.301. \]

Both skew curve and normal curve are drawn on Plate 14, fig. 13. The former is at once seen to be an excellent fit. We might fairly have simplified our work by taking zero paupers as the commencement of our range, but preference was given to the more general results in order to demonstrate that they give no appreciable amount of "negative pauperism." The range determines a limit of about 15 per cent. as the greatest possible amount of pauperism. The normal curve is seen to diverge very widely from the statistics besides giving an appreciable amount (3 to 4 unions) with "negative pauperism." The point-binomial for these statistics is also figured on the plate. Its constants are \( p = 0.833, q = 0.167, n = 14.4834, c = 1.70306, \) the start of the binomial being 5.81503 to the left of the centroid-vertical: see § 5. The fit is a very close one, the mean error of ordinate = 5.37, and the suggestiveness of such results for social problems needs no emphasising.

The case is of peculiar interest, because the statistics of pauperism are known to give a definite trend to the distribution, i.e., if the statistical curve of pauperism for 1881 be compared with that of 1891, for example, the maximum frequency of the
earlier will be found at a much higher percentage. The whole frequency curve is sliding across from right to left. Now it is of interest to notice that in this, as in other cases where the trend of the variation is known à priori, the skew curve is shifted away from the normal curve in the direction in which variation is taking place with lapse of time. It is not safe at present to extend this to all biological instances, but the result suggests, for example, that there is a secular progression towards brachycephaly in Bavarian skulls (fig. 8), towards reduced antero-lateral margin in crabs (fig. 4), towards increased height in St. Louis school-girls (fig. 7), and towards long-sightedness in Marlborough School boys.* I believe most suggestive and important results might be obtained for the theory of evolution, if we only had the series of skew curves for a biological case of progressive variation in the same manner as we have for pauper percentages.

(35.) Example XV. The theoretical resolution of heterogeneous material into two components, each having skew variation, is not so hard a problem as might at first appear, and I propose to deal at length with the subject later. If there be more than two components, the equations become unmanageable. In this case however, if the components have rather divergent means, a tentative process will often lead to practically useful results. To illustrate this I propose to conclude this paper by an example of a mortality curve resolved into its chief components. By a mortality curve I understand one in which frequency of death (for 1,000, 10,000, or 100,000 born in the same year) is plotted up to age. I have worked out the resolution for English males, and for French of both sexes. The generally close accordance of the results for both cases has given me confidence in their approximate accuracy. The method adopted was the following: An attempt was made to fit a generalised frequency curve to the old age portion of the whole mortality curve, the constants of this curve being determined from the data for four or five selected ages by the method of least squares; the frequency curve so determined was subtracted from the total curve, and a frequency curve fitted by the same method to the tail of the remainder. This second component was again subtracted and the process repeated, until the remainder left could itself be expressed by a single frequency curve. The components thus obtained were added together, and a tentative process adopted of slightly modifying their constants and position, so that the total areas of the components and of the whole mortality curve coincided. It was soon obvious that no very great change either in the constants or position was permissible, if the sum of the components was to give the known resultant curve, hence I feel very confident that whatever be the combination of causes which result in the mortality curve, that curve is very approximately to be considered as the compound of five types of mortality centering about five different ages. The allied character of the results obtained for both French and English statistics confirms this view.

* Dr. Roberts' statistics, which I have reduced to skew curves, but have not reproduced in this memoir.
Professor Lexis has already suggested that the old age distribution of mortality is given by a normal curve. Now, although the rougher French statistics give a fair approximation to a normal curve, this is not true for English males. The curve for old age is of Type I., but for all practical purposes it may be treated as one of Type III. Whatever be the chief causes of old age mortality, they extend very sensibly through middle life, and less sensibly through youth, only becoming inappreciable in childhood. Hence, if we speak of our first component as the "mortality of old age," the name is to be understood as referring to a group of causes especially active in old age mortality, but not excluded from other portions of life. The second and third components I found to be skew curves, but so nearly normal that to my degree of approximation no stress could be laid on the skewness obtained. The fourth component was a markedly skew curve, also closely given by a curve of Type III., and corresponding in general shape to the mortality curves of fevers peculiarly dangerous in childhood (e.g., diphtheria, scarlet fever, enteric fever, &c.). These three components I have termed respectively the mortality of middle life, of youth, and of childhood. I found it impossible to fit the remainder of the original mortality curve with any type of generalised curve, so long as I supposed the mortality frequency to commence with birth. I was therefore compelled to suppose the set of causes giving rise to "infantile mortality" extended into the period of gestation, and I obtained a satisfactory fit for the infantile mortality frequency, when the range of the curve started about '75 of a year before birth. The form taken by the curve is the extreme type in which the curve is asymptotic to the ordinate of maximum frequency (cf. Examples X.-XII.). The five fundamental components of the mortality curve for English males are the following, the numbers referring to 1000 contemporaries, or persons born in same year:—

(A.) Old Age Mortality.

Total frequency = 484.1.

Centroid-vertical at 67 years.

Maximum mortality = 15.2 at 71.5 years.

The equation is†

\[ y = 15.2 \left(1 - \frac{x}{35}\right)^{7.535} e^{-21.55x}, \]

the axis of \( y \) being the maximum ordinate and the positive direction of \( x \) towards age. The skewness of the curve = 343, and its range concludes at 106.5 years.

The corresponding French component = 411, but the maximum mortality (16.4) occurs at 72.5 years.

* 'Zur Theorie der Massenerscheinungen in der menschlichen Gesellschaft,' § 46. Freiburg, 1877.
† Unit of \( x = 1 \) year, unit of \( y = 1 \) death per year.
(B.) Mortality of Middle Life.

Total frequency = 173.2.
Centroid-vertical at 41.5 years.
Maximum mortality = 5.4.

The curve is very approximately normal, and has a standard deviation of 12.8 years. The corresponding French component = 180 deaths, standard deviation 12 years, with a maximum of 6 at 45 years.

(C.) Mortality of Youth.

Total frequency = 50.8.
Centroid-vertical at 22.5 years.
Maximum mortality = 2.6.

The curve is very approximately normal, with a standard deviation of 7.8 years. The corresponding French component gives a total mortality of 78, standard deviation of 6 years, and a maximum of 5.2 at 22.5 years.

The greater and more concentrated French mortality of youth is noteworthy.

(D.) Mortality of Childhood.

Total frequency = 46.4.
Centroid-vertical at 6.06 years.
Maximum mortality = 9 at 3 years.

The equation to the curve, the axis of y being maximum ordinate, is

\[ y = 9 (1 + x)^{3.77} e^{-3.77x}. \]

Thus the skewness of the curve = .87, and the range commences at 2 years.

The French component appears to be shifted further towards youth. It gives a total of 47 deaths, centroid at 8.75 years, and a maximum of 5.8 at 5.75 years, skewness = .71. Childish mortality is therefore, if these results be correct, more concentrated, and at an earlier age in England than in France.

(E.) Infantile Mortality.

Total frequency after birth = 245.7.
Maximum frequency after birth occurs in first year and equals 156.2.

The equation to the frequency curve is

\[ y = 236.8 (x + .75)^{-3} e^{-7.8x}, \]

the origin being at birth, the skewness .707, and the centroid at .083 year, = 1 month nearly, before birth. Taking the corresponding French component, we have a total frequency after birth of 284, with 186 deaths in the first year of life. Infantile mortality is therefore considerably greater in France.

* The mortality of youth would be better expressed by a curve of type \( y = y_0 \left(1 - \frac{x^2}{\alpha^2}\right)^m \): see our § 13 (v.).
If we investigate the areas of our infantile mortality curve, we have the following deaths:

<table>
<thead>
<tr>
<th>Year of Life</th>
<th>Theory</th>
<th>Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st year</td>
<td>156.2</td>
<td>158.5</td>
</tr>
<tr>
<td>2nd year</td>
<td>53.5</td>
<td>51.2</td>
</tr>
</tbody>
</table>

After this the mortality of childhood begins to sensibly increase the infantile mortality. Turning to the "antenatal" portion of the curve, we have the following results, of course not verifiable from ordinary mortality statistics:

(i.) The total "antenatal" deaths for the 9 months preceding birth are 605 for every 1000 actually born and registered.

(ii.) "Antenatal" deaths for the 6 months immediately preceding birth are 214 for every 1000 born.

(iii.) "Antenatal" deaths for the 3 months immediately preceding birth are 83 for every 1000 born at the proper period.

The 391 "deaths" of the first three months of pregnancy would not be recorded, and in many cases possibly pass without notice. The 214 deaths of the remaining six months would be considered as miscarriages or still-births. The proportion of 1 in 6 of such accidents to births of the normal kind does not appear excessive. On the average Dr. Galapin says such an occurrence is "the experience of every woman who has borne children and reached the limit of the child-bearing age." So far then there appears nothing to contradict our theoretical results in what is known of the first six months of antenatal life.

For the last three months we have more definite data. According to our curve we have 83 deaths (per 1000 born) in the last three months before birth, or 83 in 1083 pregnancies = about 7.7 per cent. Now this percentage must consist of two factors—still-born children and children who, born before their time, die shortly after birth, and who would not be recorded in any proper proportions in statistics based on census returns, nor as a rule in the returns of maternity charities.

For statistics of still-births, I find:

- Dublin Rotunda Hospital (1847–54) 6.9 per cent.
- J. H. Davis for 14,000 births in St. Pancras 6.1 per cent.
- Guy's Hospital Lying-in Charity, 25,777 births, 1,127 born dead or died within a few hours, 1000 corresponding to births in the last three months of pregnancy 3.84 per cent.
- Newsholme's "Vital Statistics" (no authority cited) 4 per cent.
It would thus appear that there are 4 to 5 per cent. of still-births, thus leaving 2.7 to 3.7 per cent. of deaths to be accounted for—if there is any validity in our analysis—by deaths of children born before their proper time and dying before their proper birthdays. Such deaths would not appear in the category of still-born children in the returns of the maternity charities, nor in any true proportion in the census returns.

Thus, while it is impossible to assert any validity for the antenatal part of our curve of infantile mortality, while, indeed, the constants of that curve, and consequently the percentages of antenatal deaths, might be considerably modified had we surer data of the actual deaths in the first year of life; still there appears to be nothing wildly impossible in the results obtained, and they may at any rate be suggestive, if only as to the nature of those statistics of "antenatal" deaths, which it would be of the greatest interest to procure.

The absolute necessity of skew curves in all questions of vital statistics is sufficiently evidenced in this resolution of the general mortality curve. A complete picture of the resolution into components of the mortality curve is given (Plate 16, fig. 18), with a separate figure on an enlarged scale of infantile mortality.

(36.) In conclusion, there are several points on which it seems worth while to insist. The normal curve of errors connotes three equally important principles:

(i.) An indefinitely great number of "contributory" causes.

(ii.) Each contributory cause is in itself equally likely to give rise to a deviation of the same magnitude in excess and defect.

(iii.) The contributory causes are independent.

The frequency of each possible number of heads in repeatedly throwing several hundred coins in a group together, practically fulfils all the above three conditions.

Condition (ii.) is not, however, fulfilled if a number of dice be thrown or a number of teetotums of the same kind be spun together. Condition (iii.) is still fulfilled.

Condition (iii.) is not fulfilled if $p$ cards be drawn out of a pack of $nr$ cards containing $r$ equal suits, supposing the $p$ cards to be drawn at one time. Now, it appears to me that we cannot say $a$ priori whether the example of tossing, of teetotum-spinning, or of card-drawing is more likely to fit the proceedings of nature. There is, I think, now sufficient evidence to show that the conditions (i.) to (iii.) are not fulfilled, or not exactly fulfilled, in many cases—in economic, in physical, in zoometric, and botanical statistics. We are, therefore, justified in seeing what results we shall obtain by supposing one or more of the above conditions which lead to the normal curve to be suspended. The analogy of teetotums and cards leads us to a system of skew frequency curves which in this paper have been shown to give a very close approximation to observed frequency in a wide number of cases—an approximation quite as close as the writer has himself obtained between theory and experiment in very wide experiments in tossing, card-drawing, ball-drawing, and
lotteries. But the introduction of these skew curves leads us to two important conclusions:—

(i.) If a material be heterogeneous we have no right to suppose it must be made up of groups of homogeneous material each obeying the normal law of distribution. Each homogeneous group may follow its own skew distribution.

(ii.) If material obeys a law of skew distribution, the theory of correlation as developed by Galton and Dickson requires very considerable modification.

We may note two points bearing on these two conclusions, which do not seem without interest for the general problem of evolution. Fever mortality curves are skew curves. The general mortality curve—frequency of death at different ages—is a compound of many diseases, but with sufficient approximation, it can be resolved into five components; three of these components are markedly skew, the other two less so. Selection, according to age, is thus distributed with different degrees of skewness about five stages in life; this at least suggests that selection according to the size or weight of an organ may be compound, if we take a considerable range of size, and that the components may have varying degrees of skewness.

The correlation of the ages of husband and wife at marriage is a subject with regard to which we have a very fair amount of material. For a given age of the husband, the frequency of marriage with the age of the wife fits very closely a curve of Type IV., and with sufficient exactness very often a curve of Type III.* The sections of the surface of frequency are oval curves differing entirely from the ellipses of the Galton-Dickson theory, but resembling in general the “oval” polygons obtained by taking horizontal sections of the frequency polyhedron for the correlation of cards of the same suit in two players’ hands at whist. Plate 9, fig. 19, shows how widely these differ from ellipses. There seems therefore to be considerable danger in assuming in vital statistics, whether in man or the lower animals, that the “contributory” causes are independent. All the statistics for sizes of organs in animals, which I have yet analysed, if they are not compound, seem to agree in following a curve of Type IV., and suggest this kind of inter-dependence of the “contributory” causes. Their correlation surfaces of frequency will thus have for lines of level skew ovals—what for want of a better name may be termed “whist ovals” as distinguished from the ellipses which flow from the normal frequency surface. The remarks from quite a different standpoint of Ranke on skull measurements seem to lead to the same conclusion. I propose on another occasion to illustrate the resolution of compound curves into skew components, and further to deal with the main features of correlation in cases of a skew frequency distribution.

* I have fitted some of Percozzi’s marriage statistics with skew curves, but reserve their discussion for the present, as they belong properly to the theory of skew correlation.
MR. DOUBT TO GIVEN. (x).

Note.

Added May 24, 1895.

[Since writing the above memoir my attention has been drawn to a note in Dr. Westergaard’s “Theorie der Statistik,” referring to Professor T. N. Thiele’s treatment of skew frequency curves. I have procured and read his book, ‘Forelaesninger over Almindelig Iagttagelseslaere,’ Kjøbenhavn, 1889. It seems to me a very valuable work, and is, I think, suggestive of several lines for new advance. It does not cover any of the essential parts of the present memoir. Dr. Thiele does indeed suggest the formation of certain “half-invariants,” which are functions of the higher-moments of the observation—quantities corresponding to the $\mu_4 - 3\mu_2^2$, $\mu_5 - 10\mu_2\mu_3$, &c., of the above memoir. He further states (pp. 21–2) that a study of these half-invariants for any series of observations would provide us with information as to the nature of the frequency distribution. They are not used, however, to discriminate between various types of generalised curves, nor to calculate the constants of such types. A method is given of expressing any frequency distribution by a series of differences of inverse factorials with arbitrary constants. Thus if

$$\beta_n(x) = \frac{|n|}{x^{|n|}}$$

and

$$\Delta\beta_n(x) = \beta_n(x + \frac{1}{2}) - \beta_n(x - \frac{1}{2})$$

we can express any law of frequency $y = f(x)$ by

$$f(x) = b_0\beta_n(x) + b_1\Delta\beta_{n-1}(x) + \ldots + b_n\Delta^n\beta_0(x),$$

where the constants $b_0, b_1 \ldots b_n$ can be determined numerically when the frequency of $n + 1$ chosen derivation-elements is known.

I see a possibility of more than one theoretical development of interest, especially in relation to compound material, from this development of Dr. Thiele’s, but I doubt whether it can be of practical statistical service even as an empirical expression for frequency. Instead of having the 3 to 5 constants of our generalised curves, the full value of Dr. Thiele’s expression requires as many constants as there are recorded frequencies, and then expresses the result in functions like $\Delta^n\beta_n(x)$, by no means easily realised or likely to appeal to the practical statistician. It is true the complete series gives absolutely accurately the frequency of all the points used in the calculation, but it does not, like the generalised curves, indicate the purely accidental variations of the frequency. If, on the other hand, we take, as Dr. Thiele suggests, some half-dozen terms only of the series—which give the really essential character of the
frequency—we obtain results which, although more complex in form, are not as satisfactory as those given by the generalised curve.

For example, Dr. Thiele gives the following series (p. 12):

<table>
<thead>
<tr>
<th>Values</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>3</td>
<td>7</td>
<td>35</td>
<td>101</td>
<td>89</td>
<td>94</td>
<td>70</td>
<td>46</td>
<td>30</td>
<td>15</td>
<td>4</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

His "Faktiske Fejllove" gives

\[
y = 1.221\beta_{12}(x) + 278\Delta^2\beta_{11}(x) + 600\Delta^3\beta_{10}(x) \\
+ 216\Delta^3\beta_9(x) + 278\Delta^4\beta_8(x) - 318\Delta^5\beta_7(x) \\
+ 574\Delta^6\beta_6(x) + 596\Delta^7\beta_5(x) + 499\Delta^8\beta_4(x) \\
+ 259\Delta^9\beta_3(x) - 0645\Delta^{10}\beta_2(x) - 0303\Delta^{11}\beta_1(x) \\
- 0088\Delta^{12}\beta_0(x).
\]

He tells us that 6 terms practically suffice, the additional terms merely accounting for the individual irregularities of this particular 500 observations. Without specifying what the observations are, he tells us that the possible values run from 4 to 28, or that the range is really limited.

If we fit our generalised curve of Type I., we find for its equation:

\[
y = 98.801\left(1 + \frac{x}{4.5191}\right)^{3.87785} \left(1 - \frac{x}{20.0296}\right)^{17.2785},
\]

the origin is at 11.191, or the range runs from 6.6715 to 31.1202, i.e., is a range of 24.5487 instead of 25, but is shifted some 2 to 3 units. Considering the small number of observations, this is not a bad approximation to a marked feature of the distribution not indicated on the surface by the observations, nor discoverable from the "Faktiske Fejllove."

Comparing our curve (i.) with (ii.) the actual statistics—all 13 terms of the "Faktiske Fejllove" series, and with (iii.) the first 6 terms of the same series, we have the following results:

<table>
<thead>
<tr>
<th>Values .</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i.) .</td>
<td>1</td>
<td>10</td>
<td>42</td>
<td>80</td>
<td>99</td>
<td>92</td>
<td>70</td>
<td>48</td>
<td>29</td>
<td>15</td>
<td>6</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>(ii.) .</td>
<td>3</td>
<td>7</td>
<td>35</td>
<td>101</td>
<td>89</td>
<td>94</td>
<td>70</td>
<td>46</td>
<td>39</td>
<td>15</td>
<td>4</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>(iii.) .</td>
<td>1</td>
<td>11</td>
<td>40</td>
<td>82</td>
<td>103</td>
<td>92</td>
<td>70</td>
<td>48</td>
<td>26</td>
<td>13</td>
<td>8</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

The generalised curve here gives slightly the better results in addition to its more easily realised form, and its fewer constants (iv.).
On the other hand, there are, I think, some points of first-class theoretical importance in the mode adopted by Dr. Thiele for expressing frequency; it gives us a means of expanding all varieties of frequency curves in a series of factorial functions which may lead to important theorems in the analysis of heterogeneous material.

Plates.

The scale of the accompanying figures is not that of the original drawings, and the clearness and distinctness of the several curves of the same figure have been, in several instances, partially lost by the process of reproduction and reduction. In every case the square element of the figure corresponds to the square centimetre of the original diagram, and is spoken of both in the text of the memoir and on the figures themselves as a square centimetre. The scale of actual reduction is indicated by a fraction placed at the lower right-hand corner of the figure.
Fig. 3.

CURVE OF BAROMETRIC HEIGHTS. 450 OBSERVATIONS.

Representation by Point-Binomial.

Point-Binomial:

I. Weighted Ordinates.

<table>
<thead>
<tr>
<th>O r d i n a t e s</th>
<th>$O_n$</th>
<th>$O_n$</th>
<th>$O_n$</th>
<th>$O_n$</th>
<th>$O_n$</th>
<th>$O_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_1$</td>
<td>$O_2$</td>
<td>$O_3$</td>
<td>$O_4$</td>
<td>$O_5$</td>
<td>$O_6$</td>
<td>$O_7$</td>
</tr>
<tr>
<td>$O_8$</td>
<td>$O_9$</td>
<td>$O_{10}$</td>
<td>$O_{11}$</td>
<td>$O_{12}$</td>
<td>$O_{13}$</td>
<td>$O_{14}$</td>
</tr>
</tbody>
</table>

II. Rectangles:

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>$R_5$</th>
<th>$R_6$</th>
<th>$R_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_8$</td>
<td>$R_9$</td>
<td>$R_{10}$</td>
<td>$R_{11}$</td>
<td>$R_{12}$</td>
<td>$R_{13}$</td>
<td>$R_{14}$</td>
</tr>
</tbody>
</table>

III. Rectangles:

<table>
<thead>
<tr>
<th>$R_{15}$</th>
<th>$R_{16}$</th>
<th>$R_{17}$</th>
<th>$R_{18}$</th>
<th>$R_{19}$</th>
<th>$R_{20}$</th>
<th>$R_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{22}$</td>
<td>$R_{23}$</td>
<td>$R_{24}$</td>
<td>$R_{25}$</td>
<td>$R_{26}$</td>
<td>$R_{27}$</td>
<td>$R_{28}$</td>
</tr>
</tbody>
</table>

Observations:

Scale of Frequency: 0.0 cm to 15.0 cm per Observations.

Fig. 4.

WELDON'S MEASUREMENTS OF THE CARAPACE RIGHT ANTEROLATERAL MARGIN OF 299 FEMALE NAPLES CRABS. (See J.B. Proc. 1893, 327)

Curve of Type II:

$$ y = 15000 \left(1 + \frac{x}{15000}\right) $$

Curve of Type III:

$$ y = 14000 \left(1 + \frac{x}{15000}\right) $$

Origin of Type II: 0.1507

Origin of Type III: 0.1507

Scale of Frequency: 0.0 cm to 15.0 cm per Individuals.

Normal Curve:

Maximum Ordinate = 0.0125

Standard deviation = 0.0245

Closest Binomial Polygon:

$$ y = 0.000 \left(1 + \frac{x}{2000} - \frac{x^2}{2000^2}\right) $$

Origin of horizontal scale = 0.5 cm of body length

Mean = 0.5 cm of body length.
Fig. 6.

CURVE OF BAROMETRIC HEIGHTS. 4857 OBSERVATIONS. (D'Venn: "Nature" Sept 1st 1895.)

Scale of Frequency: 1 cm = 500 Observations
Area = 2.15 sq. cm

Ratio of Moments about Central Vertical to Area:
- Second: 6.5 cm
- Third: 43.9 cm
- Fourth: 423.2 cm

Curve I, Doubly-Limited Range: (6549 - 50.50)
\[ y = 2 \times 6549 \left( 1 - \frac{x}{6549} \right)^2 \]

Curve II, Simply-Limited Range: (Below 50)
\[ y = 2 \times 6549 \left( 1 - \frac{x}{6549} \right)^2 \]

Origin in both cases at maximum ordinate.

Normal Curve:
- Standard Deviation = 2.434
- Maximum Ordinate = 0.6

Fig. 7.

HEIGHTS OF 2192 ST LOUIS SCHOOL-GIRLS, AGED 8 YEARS (W.T. Porter).

Equation to Curve of Type B:
\[ x = 0.0274 \text{ inch} \]
\[ y = 0.00233 \times 0.00033 = 0.0000071 \]

Observations:
- 350

Scale of Frequency: 1 cm = 50 girls

Normal Curve:
- Scale of Deviation from units
- Maximum Ordinate = 5.0

- 500

- 50

- 100
Fig. 8.

LENGTH-BREADTH INDEX OF 500 MODERN "ALT-BAYERISCH" SKULLS. (J. Ranke)

Observations:

Curve of Type B:

\[ y = e^{a+b} x \]

Distance of Maximum from Origin:

Scale of Frequency: 1 sq. cm. = 1 shuttle.

Normal Curve:

Standard deviation = 0.268
Maximum Ordinate = 164.53
Mean Index = 83.07

Fig. 10.

251 GUESSES AT A MID-TINT.

Smoothed Observations:

Curve of Type I, Range given:

Equation:

\[ y = 50 + 5 x - x^2 \]

Scale of Frequency:

Logarithmic normal.

Fig. 12.

DISTRIBUTION OF 109,566 DIVORCES ACCORDING TO DURATION OF MARRIAGE, UNITED STATES, 1882-86 (W. J. Wilcox)

Scale of Frequency: 1 sq. cm. = 5,000 divorces.

Curve of Type M:

Distribution shown in Fig. 11.

Duration of Marriage in Years.
Fig. 13.

NUMBER AND VALUE OF HOUSES. (Goschen)

Equation of the Frequency-Curve:

\[ y = 100000 \left( e^{-0.0002x} + 0.0002x \right) \]

Histogram: Theory ——
Statistics: 

Value of Minimum Value: 100
Value of Maximum Value: 10000

Total Number of Houses Under 100
Theory: 100000
Statistics: 100000

Above 100 (Theory): 1000
Statistics: 2000

Fig. 17.

STATISTICS OF PAUPERISM, ENGLAND AND WALES. DISTRIBUTION OF 632 UNIONS, 1891.

Statistics:
Curve of Type 1: ———
Equation: \[ y = 0.0005 \left( 1 - e^{-0.0002x} \right) \]
Standard Deviation: 2.3
Normal Curve: ———
Standard Deviation: 2.3
Maximum Ordinate: 100

——— Point Bimodal.
FOREHEADS OF NAPLES CRABS.

(Weldon)

Vertical scale: 2 mm = one individual.

Observations.
Compound curve (Phil. Trans. vol. 185, plate 1).
Symmetrical curve, Type 1.

Equation: 

\[ y = a \cos \left( a \frac{x}{b} \right) \times \sec b \]

Origin at \( x = 0 \) of horizontal scale.

Scale: 2 mm = 1 cm of body length.

Fig. 11.

NUMBER OF DORSAL TEETH ON ROSTRUM OF 915 PRAWNS, \( \delta \) AND \( \varphi \).
(Plymouth, Weldon).

Observations:
Normal Curve:

Maximum Ordinates: 912
Standard Deviation: 44

Shew Curve, Type \( B' \):

Equation:

\[ y = a \cos \theta \times \sec \theta \]

where \( \log y = 10 + \cos 10 \).

Origin to Centroid Vertical = 1 cm.

Fig. 18.
Fig. 18.

ENGLISH MORTALITY. MALES. DEATHS PER ANNUM OF 1000 PERSONS BORN IN THE SAME YEAR. (Ogle: 1871-1880)

Statistics: *** Compound Curve: --- One Death = \( \Box \) - 25 square.

Replotted Infantile Mortality. Frequencies to .% scale, Years to x Times scale of lower figure.

Infancy: \( y = .056 \times \frac{a}{a^2} \)

Infant mortality per thousand Census Births. Deaths in first year of Life: Theory \( 750 \) Statistics \( 1500 \).

In 4 months before Birth: \( 15 \)

\( \frac{y}{20} \) months before Birth: \( 15 \)

Origin, 1st year before birth. Centroid at one month before birth, \( TM = 25 \) years after birth.

Childhood: \( y = .026 \times \frac{a}{a^2} \)

\( \frac{y}{20} \) years. Shown in graph.

TM = 25.

Old Age: \( y = .015 \times \frac{x}{a^2} \)

\( TM = 10 \) years. Shown in graph.

Normal Curve: \( y = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \)

Normal Curve: \( y = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \)

TM = 80.

Central Points: - Axes of \( y \) — Origines = \( O_1, O_2, O_3 \), etc.

Years of Age at Death.

TM = Total Mortality. SD = Standard Deviation. \( \sigma \) = Standard Deviation.

Centroid Verticals: - Axes of \( y \) — - Origins = \( O_1, O_2, O_3 \), etc.
XI. A Determination of the Specific Heat of Water in Terms of the International Electric Units.

By Arthur Schuster, F.R.S., Langworthy Professor of Physics at the Owens College, Manchester, and William Gannon, M.A., Exhibition (1851) Scholar, Queen's College, Galway.

Received November 13,—Read November 22, 1894.

This research was originally undertaken by Professor Schuster and Mr. H. Hadley before the authors were aware that Mr. E. H. Griffiths was engaged on a similar investigation. After a number of preliminary experiments, and just as the final arrangements for the conduct of the measurements were being definitely made, Mr. Hadley, on his appointment to the Head Mastership of the School of Science and Art, Kidderminster, had to leave Manchester. In the meantime Mr. Griffiths' important research was published; and we had to consider whether our own work, which was designed on a smaller scale, could compete with it in accuracy. We decided to complete the investigation, principally for the reason that, although we both aimed at determining what is commonly called the mechanical equivalent of heat through the heating of a certain mass of water by means of an electric current, the details of the experiments differed very materially, so that our two ways of dealing with the problem seemed to afford a useful test of the amount of agreement which may be obtained at present. Our investigation touches only a small part of that treated by Mr. Griffiths, as we did not attempt to measure the changes in the specific heat of water due to change of temperature. On the other hand, the more modest limits within which we have confined ourselves, allowed us to use a much simpler apparatus. On Mr. Hadley's departure, Mr. W. Gannon took his place. From the former gentleman we received a good deal of help in the devising and construction of some important parts of the apparatus.

The principle of the method we have used is extremely simple. The electrical work done in a conductor being measured by $\int EC\,dt$, where $E$ is the difference of potential at the ends of the conductor, $C$ the current and $t$ the time, we keep the electromotive force constant, and measure $\int C\,dt$ directly by a silver voltameter. We do not therefore require to know the resistance of the wire, and we thus avoid the difficulty of having to estimate the excess of temperature of the wire over that of the water in which it is placed. We also gain the advantage of not having to measure time, and therefore are able to complete the experiment more quickly than 19.7.95.
we could have safely done if the length of time during which the current passed had to be measured with great accuracy.

As regards the dimensions of the apparatus, there is not very much choice. The voltmeter limits the current intensity to about one ampère. The calorimeter must contain at least one litre of water, otherwise the corrections for cooling become too large; on the other hand difficulties of stirring appear when the mass of water is too great; the calorimeter in our experiments contained about 1500 grams of water. In order to measure the rise in temperature of the water with sufficient accuracy, that rise should not be less than 2°; and it is easily calculated that if the experiment is to be completed in about ten minutes, the electromotive force—with the current and the quantity of water fixed upon—must be about thirty volts. We used Clark cells as our standard of electromotive force, and a battery of twenty cells was found sufficient for our purpose. Having fixed on the current and electromotive force, the resistance of the wire can be determined.

The accuracy which can be obtained altogether depends on the attention given to small details, and we therefore proceed to describe separately the various parts of the apparatus used.

The Clark Cells.

As standard of electromotive force we used Clark cells. It was originally intended to keep one of these cells at a constant temperature of about 25° C. in a thermostat. This cell (fig. 1), which we shall call the C.T.C. (constant temperature Clark), was constructed according to a pattern which has proved very useful when it is desirable to have a cell which can stand without damage a moderate current for a short time. A small Woulfe's bottle is taken in which the three openings have stoppers made of glass ground into the necks. The stopper fitting into the central opening has a platinum wire fused into it, and the zinc rod is attached to this wire. Of the two other openings, one carries a bent tube with a mercury trap, and the other a glass tube which passes to the bottom of the bottle. A platinum wire passes through this tube and dips into the mercury. The mercury trap is useful in the early history of the cell, as it is difficult to avoid generation of some gas at first, and the additional pressure thus produced often damages the joints of the cell. After a time the mercury may be removed, and the tube sealed off. The cells were set up with the usual precautions, and have now worked for some years satisfactorily. There is, of course, the usual difficulty of ascertaining the temperature; thermometers have been inserted into some of them, but even then, though they have proved of great utility, they are not suitable as standards when great accuracy is required, unless placed in an enclosure of constant temperature.

The comparison of our Clark cells was always made by opposing them and measuring the difference of their electromotive forces. For this purpose the current from a Leclanché cell (L, fig. 5, p. 427) was passed through a fixed resistance (R) of 10,000
DETERMINATION OF THE SPECIFIC HEAT OF WATER.

Fig. 1.

Mercury trap.
Zinc rod.
Platinum wire in glass tube.
Saturated solution of zinc sulphate
Paste of mercurous sulphate.
Pure mercury.

Fig. 2.

Thermometer.
Saturated solution of zinc sulphate.
Mercurous sulphate.
Zinc amalgam.
Pure mercury.
ohms and through a resistance box. The difference in the potential at the terminals of this box was balanced in the usual way by the residual electromotive force of the two Clark cells. If \( e_1, e_2, E \) be the electromotive forces of the Clarks and the Leclanché respectively, and \( r \) the resistance of the box when there is a balance,

\[
e_1 - e_2 = E \frac{r}{10000 + r}.
\]

When two Clarks which have approximately the same temperature are compared, \( r \) would be equal to only a few ohms, and in that case we may neglect the \( r \) in the denominator, and in many cases take the electromotive force of the Leclanché equal to that of the Clark. Care was taken that the Leclanché cell had its normal electromotive force, which was measured whenever any change in its value might have produced an appreciable difference in the experiments.

Large cells can only be used as standards, if they are constructed according to the principle of Lord Rayleigh's H cell. In the spring of 1891 a cell was set up having the form of fig. 2. It consists of two glass vessels, one being placed inside the other. The outer vessel contains the zinc amalgam, the inner vessel the mercury. The vessel is covered by a wooden lid, through which the electrodes and a thermometer are passed. The upper part of the outer vessel is paraffined so as to prevent the creeping of the zinc sulphate over the sides. Very little evaporation takes place, and the lid is readily removed so that the cell may be refilled when necessary. It was constructed originally so that the liquid could be stirred, but it was found better not to disturb the cell. This cell has answered all requirements perfectly, and will be referred to as the "standard." The cell, which is not readily moved owing to its weight, stands in a corner of a small cupboard, and was compared at intervals with the C.T.C. between November, 1891, and June, 1892. The results are given in Table I. The thermostat, which was not adapted for temperatures as low as 25° C., had to be readjusted occasionally, hence the small variation in temperature shown in the second column. The temperature of the standard at different times varied between 11°.2 C. and 18°.3 C., and the experiments afford a good test as to the limits within which a temperature correction could be safely applied.
DETERMINATION OF THE SPECIFIC HEAT OF WATER.

Table I.—Comparison of Standard Clark Cell with C.T.C. Cell.

<table>
<thead>
<tr>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
<th>5.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Temperature in thermostat.</td>
<td>Temperature of standard.</td>
<td>Observed difference reduced to 25°C.</td>
<td>Calculated difference.</td>
</tr>
<tr>
<td>1891. Nov. 26</td>
<td>25.26</td>
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<td>-67</td>
</tr>
<tr>
<td>Dec. 11</td>
<td>25.3</td>
<td>13.8</td>
<td>-68</td>
<td>-68</td>
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<tr>
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<td>25.4</td>
<td>11.9</td>
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<td>-82</td>
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<tr>
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<td>25.08</td>
<td>14.1</td>
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<tr>
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<td>-66</td>
<td>-66</td>
</tr>
<tr>
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<td>11.2</td>
<td>-87</td>
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<tr>
<td>May 5</td>
<td>25.7</td>
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<td>-69</td>
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<tr>
<td>May 9</td>
<td>25.4</td>
<td>15.9</td>
<td>-33</td>
<td>-63</td>
</tr>
<tr>
<td>June 24</td>
<td>25.32</td>
<td>14.8</td>
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<td>-60</td>
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<tr>
<td>June 1</td>
<td>25.46</td>
<td>18.3</td>
<td>-34</td>
<td>-34</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td>13.99</td>
<td>-66.3</td>
<td></td>
</tr>
</tbody>
</table>

A small correction to the observed numbers is necessary, owing to the small variations in temperature of the C.T.C. cell. The corrected values of \( r \) are given in the fourth column. As the C.T.C. cell was not quite saturated with zinc sulphate when placed in the thermostat, the temperature coefficient '0004 was used to reduce its value to 25°C. The corrections are so small that an accurate knowledge of that coefficient is not required. The mean temperature of the standard cell in all these experiments was 13.99, the mean value of \( r \) was 66.3. From these data we may calculate what the value of \( r \) should have been in each experiment, on the assumption that the temperature coefficient of the standard was '00081. The values of \( r \) thus deduced, are given in the fifth column. With the exception of the experiment on May 20, the agreement is quite satisfactory; and we are justified in concluding that the changes in the electromotive force of our standard cell may be correctly deduced

* The temperature coefficient determined by Glazebrook and Skinner (Phil. Trans., vol. 183, 1892, A) is '00076 between 0° and 15°—that is, for an average temperature of 7.5°. The temperature coefficient according to Kahle (Zeitschrift für Instrumentenkunde, August, 1893) is -'000814 - '000007 \((t-15)\), giving an identical value for \( t = 7.5°. \)
from the readings of the thermometer placed in it. Recent results of Kahle agree with our conclusions, and show that, in the H form of cell, the lag in the change of the electromotive force with change of temperature is avoided, owing to the fact that the liquid at both electrodes, being in contact with crystals of zinc sulphate, is always in a state of concentration. We have, after the conclusion of our experiments, set up a few cells according to the instructions given in the Third Memorandum of the Board of Trade. When proper precautions are taken to ensure equality of temperature, these cells agree within about one part in ten thousand with each other and our standard cell. Taking account of the determination by Glazebrook and Skinner of the electromotive force of a Clark cell—1·4342 at 15° C.—and of the slightly lower value obtained by Kahle, we have adopted 1·4340 as the value of our standard cell in terms of the international volt. As temperature coefficient, we have adopted that given by Kahle (see footnote on preceding page).

Fig. 3.

Arrangement for Comparison of Clark Cells.

The electromotive force at the ends of the heating coil in our experiments had to be kept balanced against twenty Clark cells. These cells form part of a battery of one hundred cells constructed in the year 1890, about eighty of which are still in good condition. A set of twenty is mounted in two rows of ten each. The cells are small, but as we had no means of keeping their temperature constant, their combined electromotive force had, whenever required, to be determined in terms of the standard cell. This could be quickly done as follows:—Ten cells of the form shown in fig. 1 were placed side by side in the same cupboard that contained the standard cell (fig. 3 and c.c., fig. 5). The terminals of these cells—which we shall call the "Cupboard Clarks"—were permanently connected to mercury cups numbered 1, 2, &c. (fig. 3). A board of wood was placed in front of the Clarks and contained a series of cups 1', 3', 5', &c., permanently connected by copper strips, and a second series 2', 4', 6', similarly connected. The cups of the two series were placed respectively opposite the positive and negative poles of the Cupboard Clark cells and
could be connected to them by means of copper bridges A and B. The standard cell being inserted and the two bridges being placed as shown in the figure, the Cell II. is opposed to the standard and the difference of their electromotive force is measured. Moving the bridges along from one set of cups to the next, the ten Cupboard Clarks may be rapidly interchanged.

The mounting of the cells also allows of their being rapidly placed in series by means of copper strips. The figure shows the Cells III., IV., V. thus connected. The galvanometer used in these comparisons (G, fig. 5) was one of Lord Kelvin’s High Resistance Astatic Galvanometers. Its resistance was 5600 ohms. It was placed on paraffin blocks for better insulation. During use its sensitiveness was such that one scale division corresponded to $7.3 \times 10^{-6}$ volt. A carbon resistance (P, fig. 5) could be thrown into series with the galvanometer when it was necessary to diminish its sensitiveness. A commutator (K, fig. 5) served to change rapidly the circuit in which the galvanometer was inserted. This commutator was made of a paraffin block containing seven mercury cups, but two sets of two were permanently connected as shown in the figure. Three copper bridges served to connect temporarily the terminals $s$ to $g$, $g$ to $j$ or $k$, $s'$ to $p$ or $q$; when $s$ was connected to $g$ the Standard Clark was opposed to one of the ten Cupboard Clarks. When the ten Cupboard Clarks were to be opposed to one half of the battery of twenty cells, $g-j$ and $s'-p$ were connected; for the other half $g-k$ and $s'-q$ were joined. In the equivalent experiments when the battery had to be opposed to the electromotive force at the end of the heated coil, the three temporary bridges were removed.

The operation of standardising the electromotive force of our battery took about ten minutes and was carried out as follows:

1. Reading of the thermometer placed in the Standard Clark, $t'_1$.

2. Comparison of the ten Cupboard Clarks separately with the Standard. The comparison of Cell I. with the Standard gives us a relation of electromotive forces which may be written

$$I. - \text{Standard} = a_1,$$

and the addition of all such relations gives us for the ten cells

$$(I. + II. + III. + \ldots + X.) - 10 \text{ Standards} = a_1 + b_1 + \ldots = S_1.$$

3. Comparison once more of the Cell I. with the Standard gives

$$I. - \text{Standard} = a_2.$$

There may be a small difference between $a_1$ and $a_2$ owing to temperature changes.

4. Reading of the thermometers placed in the Standard, $t_2$.

5. Comparison of Sets (1) and (2) of the battery of 20 cells with the 10 Cupboard Clarks in series, giving by addition the relation

$$\text{Set (1)} + \text{Set (2)} - 2 \times (I. + II. + III. + \ldots + X.) = 2T_1.$$
6. Third comparison of the Cupboard Clark I. with the Standard, the difference being denoted by \( a_3 \).

7. Reading of the thermometer of the Standard Clark, \( t_4' \).

From the above measurements we obtain the electromotive forces of our battery in terms of the Standard, thus:

\[
\text{Set (1) + Set (2) = 20 Standards + 2 (S_1 + T_1).}
\]

After the completion of each experiment for the equivalent, the comparisons are carried out in the reverse order, and if \( S_2 \) and \( T_2 \) denote the quantities corresponding to \( S_1 \), \( T_1 \) we may take the electromotive force of the battery during the experiment to be the arithmetical mean of that determined at the beginning and end. The relation, written as above, would be

\[
\text{Set (1) + Set (2) = 20 Standards + (S_1 + S_2 + T_1 + T_2).}
\]

A small correction is necessary owing to the fact that the temperature of the Cupboard Clarks may not have been the same during their comparison with the battery as it was while they were being compared with the Standard. We may, without sensible error, assume that all Cupboard Clarks varied equally, and that, therefore, the alteration due to temperature changes, for each cell measured in electromotive force, is expressed by the difference of \( \frac{1}{2} (a_2 + a_3) \) and \( \frac{1}{2} (a_1 + a_2) \). Hence we correct for the change of the ten cells by adding to \( S_1 \) the quantity \( 5 (a_3 - a_1) \). A similar correction applies to the final comparison, so that the complete relation of electromotive force is given by

\[
\text{Set (1) + Set (2) = 20 Standards + (S_1 + S_2 + T_1 + T_2) + 5 (a_3 - a_1 + a_4 - a_6).}
\]

The temperature of the Standard to which the equation applies is the mean between \( \frac{1}{2} (t_3' + t_4') \) and \( \frac{1}{2} (t_4' + t_5' + t_4') \). The temperatures \( t_3, t_3, t_4, t_5, t_4 \) were practically identical in every case, we may take without error \( \frac{1}{2} (t_3 + t_4) \) to be the temperature of the Standard during the comparisons.

*The Silver Voltameter.*

The platinum bowl which served as voltameter had a diameter of 9 centims. and a greatest depth of 4 centims. A 20 per cent. solution of the nitrate of silver was used, the salt being supplied by Messrs. Johnson, Matthey, and Co., as thrice recrystallized. The silver plate serving as anode was supplied by the same firm. It was 7 centims. in diameter and 2 millims. thick. The dish rested during the experiments on tinfoil wrapped round a ring of copper, which rested on a tripod, also covered with tinfoil (V, fig. 5). The tripod stood on paraffin blocks. The silver plate, protected
by filter-paper, was suspended from three platinum wires attached to a copper terminal. The insulation of the voltameter was amply sufficient, and the contacts were all sufficiently good to allow a perfectly steady current to pass. In order always to bring back the dish to the same condition, the silver deposit of the previous experiment was always dissolved away before a new deposit was made. The dish was washed successively with (1) concentrated nitric acid, (2) a solution of potash, (3) tap water, (4) distilled water. After drying in air-bath the empty dish was weighed two or three times with the usual precautions. The silver deposit was treated in the manner described by Lord Rayleigh. Immediately after an experiment the silver solution was removed from the dish, the deposit washed three times, and left overnight with distilled water. After washing again next morning, the deposit was dried in an air-bath, first at 100° C., subsequently the temperature of the bath was raised for 10 or 15 minutes to 160° C. The dish was then again weighed two or three times. The distilled water used in washing left no residue on evaporation from platinum foil, nor gave any visible turbidity with silver nitrate solution. The voltameter was efficiently protected from dust, which might otherwise have got entangled in the silver. The deposit always firmly adhered to the dish in characteristic radial lines, and no difficulty was ever experienced in the washing.

**Correction of the Weight to Vacuo.**

In correcting the weighings to vacuo we must distinguish between the bowl and the silver. As regards the bowl, it is only the difference in the density of the air when the two weighings are taken which will affect the result. We found it, therefore, most convenient to reduce the weighings to the normal state of the atmosphere instead of to vacuo. The correction \( k \) to vacuo may be written \( k = w p a \), \( a \) being a constant and \( p = p_0 h_1 t_0 / h_0 t_1 \), where

\[
\begin{align*}
    p_0 &= \text{density of air at 76 centims. and 15° C.}, \\
    h_1 &= \text{height of barometer at time of weighing}, \\
    t_1 &= \text{absolute temperature of balance case}, \\
    h_0 &= \text{76 centims.}, \\
    t_0 &= 288°. 
\end{align*}
\]

Representing the changes in barometric pressure and temperature by \( dh \) and \( dt \) respectively, we may express the difference in the buoyancy correction from that which would hold if the temperature was 15° C. and barometric height 76 centims. by

\[
dk = \frac{w p_0}{h_0} \left\{ t_0 dh - h_0 dt \right\}. 
\]
Substituting the values which apply to our platinum bowl weighed against brass weights, viz.,

\[ w = 64, \quad \rho_0 = 0.00122, \quad a = \frac{1}{21.5} - \frac{1}{31} = -0.0725, \]

the correction becomes

1. for difference in temperature + 0.020 \((t - 15)\) millim.
2. ,, ,, pressure + 0.074 \((76 - h_1)\) ,,

As regards the silver deposit, the correction amounts to 0.024 millim. for each gram. Neither the accuracy of our weighings nor our knowledge of the equivalent of silver render it necessary to apply so small a correction, which would alter our final result by only one part in 40,000.

The balance used was one of Oertling’s long beam balances, and the sensibility was adjusted so that with a load equal to that of the platinum bowl 1 millim. corresponded to one scale division. The bowl was always counterbalanced by the same weights before and after the deposit, so that any error in these weights would not affect the result.

To determine the correction, if any, to the weights used in balancing the silver deposit, a brass weight of nominal value of 1 gram. was standardised by the Board of Trade, and found to weigh 1.000032 gram. The silver deposit weighing always just above 0.5 gram., it was sufficient to determine the error of the 0.5-gram. platinum mass which was used in all the experiments. Four experiments gave for the corrected mass: 0.499966, 0.500020, 0.500032, 0.499998, or, as a mean, 0.50004 gram. It was therefore sufficient to assume the 0.5-gram. weight to be correct.

**The Heating Coil.**

The coil in which the electric energy was converted into heat was made of a length of 760 centims. of platinoid wire, having a diameter of 0.0345 centims. (29 B.W.G.) and a resistance of approximately 31 ohms. The coil used during the first few experiments was wound on a frame made of thin strips of ivory. On determining the specific heat of that substance we met, however, with a serious difficulty, as it was found to absorb a considerable quantity of water, which it gave up again on heating. Thus a fresh strip of ivory was found to lose 10 per cent. of its weight after heating in an air-bath for two hours. Even coating with shellac will not overcome the gradual absorption of water. Having had to discard ivory, we fixed on porcelain, and were supplied through the kindness of the Worcester Manufactory with strips of that material. The mounting of the frame and wire is seen in fig. 4.

Four strips of porcelain, 14 centims. long and 1 centim. broad, with 30 notches to keep the wire in position, are mounted by fixing their ends in sockets made of brass foil. These sockets were connected by stout brass wire. The ends of the platinoid
wire were fixed to stout copper wire about 5 centims. long wedged into the bottom of cylindrical pieces of ebonite. The ebonite was held in position by brass supports soldered to the frame. The upper ends of the copper terminals projected into the bottom of cups drilled from above in the ebonite; these holes, which were 9 millims. wide and 15 millims. deep, were filled with mercury, and served to connect the coil with the outer circuit. The coil was insulated by a covering of shellac. To obtain a thin and uniform layer, the frame was immersed in a weak alcoholic solution of the substance, and afterwards heated for half-an-hour in an air-bath at a temperature of 130° C. This process of immersion and heating was repeated until the insulation resistance was higher than that required by the conditions of the experiment, and we
were quite satisfied with the permanence of the covering obtained. The insulation was tested from time to time and the coil re-covered when necessary. When the coil immersed in water was connected to one terminal of the battery, the second terminal being a bare wire, the resistance was generally found to be over 40,000 ohms, the electromotive force being 30 volts. That an insulation resistance equal to that amount is amply sufficient will be seen if it is remembered that leakage can only cause error in so far as the water is decomposed. If the whole of the current were to pass through the water instead of through the coil, about 1 volt would be lost, so that an error of 3 per cent. only would result. Considering the small diameter of the wire and the high resistance of distilled water, it will appear that, even if our wire had been completely uncovered, the error introduced would not have been great, and even an insulation resistance of 1000 ohms would have made it inappreciable.

The Stirring.

The stirrer is shown in figs. 4 and 5. It consisted of a piece of brass foil cut to a half-moon shape. The upper surface was soldered to fine brass tubing, 17 centims. long. Two pieces of glass tubing fixed to the frame of the coil passed through circular holes cut into the stirrer and served as guides. The stirrer was moved up and down by a wheel and crank W (fig. 5) driven by an electromotor. A piece of brass tubing, of the same kind as that attached to the stirrer, was fixed to the crank, and the motion was transmitted by a flexible joint made of several layers of thin unvulcanised india-rubber, firmly tied to each of the two parts of the brass tubing. This joint, devised by Mr. Hadley, worked very satisfactorily, and allowed sufficient lateral play to facilitate the adjustment of the calorimeter and coil below the driving wheel of the stirring apparatus.

Some Questions concerning Thermometry.

The method of using mercury thermometers in accurate work has undergone considerable change in the last twenty years. In measuring a temperature, the interval between 0° and 100° used to be determined by plunging the thermometer first into a mixture of ice and water, and then into boiling water. If the two readings are \( T_0 \), \( T_{100} \), the temperature \( t \) corresponding to an intermediate reading, \( T_t \) would be

\[
 t = 100 \frac{(T_t - T_0)}{(T_{100} - T_0)} \quad \ldots \quad \ldots \quad \ldots \quad (1)
\]

Owing to certain properties of the glass envelope, analogous in their effects to elastic fatigue, a thermometer when exposed to a constant temperature will not, however, take up its final indication for a time which may be considerable, and this set of the glass affects especially the zero point, the apparent zero as at first observed
DETERMINATION

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THE

SPECIFIC

HEAT

OF

WATER.

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Fig. 5.

$K_1K_2K_3K_4K_5 = \text{Mercury keys.}$

$W_4W_5W_6 = \text{Adjustable resistances.}$

$S_1S_2 = \text{Resistance switches.}$

$A_1 = \text{Main battery.}$

$A_2 = \text{Auxiliary battery.}$

$M = \text{Current-meter.}$

$J = \text{Water-jacket.}$

$D = \text{Cover over calorimeter.}$

$W = \text{Stirrer apparatus.}$

$T = \text{Temporary coil.}$

$U = \text{Resistance in temporary circuit equal to voltameter resistance.}$

$V = \text{Silver voltameter.}$

$Q = \text{Plug key in main circuit.}$

$G = \text{Kelvin high-resistance astatic galvanometer.}$

$S.C. = \text{Standard Clark.}$

$C.C. = \text{Cupboard Clarks'.}$

$C.B. = \text{Clark battery.}$

$P = \text{Carbon resistance.}$

$r = \text{Box of 1–40 ohm coils.}$

$R = 10,000 \text{ ohms.}$

$L = \text{Leclanché cell.}$

$T_1 = \text{Principal thermometer (Baudin).}$

$T_2T_3 = \text{Auxiliary thermometer.}$
being dependent on the temperature to which the thermometer was previously exposed. It is found, however, that consistent results can be obtained by referring the reading of a thermometer not to a fixed zero, but to the position of the mercury thread, observed when the thermometer is plunged into ice directly after being exposed to the temperature to be measured. Calling \( T_0' \) the zero, as thus determined, after exposure to the temperature \( t \), that temperature measured in the mercury thermometer is now defined as

\[
t = 100 \frac{(T_t - T_0')}{(T_{100} - T_0)} .
\]  

The two definitions of temperature indicated by (1) and (2) are identical if the so-called depression of the zero \( T_0^0 - T_0' \) is proportional to the temperature \( t \), as with thermometers made of the Jena, or French standard glass. Writing in this case

\[
T_0^0 - T_0' = \alpha (T_t - T_0'),
\]

or

\[
T_t - T_0' = \frac{1}{1 - \alpha} (T_t - T_0^0),
\]

and similarly

\[
T_{100} - T_0^{100} = \frac{1}{1 - \alpha} (T_{100} - T_0^0),
\]

we obtain by substitution in (2)

\[
t = 100 \frac{(T_t - T_0^0)}{(T_{100} - T_0^0)},
\]

which is identical with (1), if the zero in that equation is meant to signify the position which the thermometer would take up if plunged into ice for a considerable time.

If the observations are made with English glass of recent manufacture, the identity of equations (1) and (2) does not hold, as the depressions of the zero are nearly proportional to the squares of the temperatures. It then becomes of importance to define clearly how a temperature is taken. Thus \textit{Wiebe} finds that thermometers made of English glass read lower than the air thermometer by as much as \( 0^\circ \cdot 047 \) at \( 40^\circ \), while \textit{Rowland} states that \textit{all} thermometers examined by him, including those of English manufacture, read higher than the air thermometer. The two statements are not contradictory; the discrepancy is explained by the fact that \textit{Wiebe} refers all temperatures to the zero observed directly after each reading, while at the time \textit{Rowland}'s work was done, this practice, which alone converts the thermometer into an instrument fit for scientific research, and is now uniformly adopted, had not yet come into use.

It is an essential point in thermometric measurements that the work done by different observers should be comparable, and some uniform scale should be adopted.
may introduce errors into a calorimetric measurement. With French or German standard glass the depression of the zero, corresponding to a certain interval, is less than the thousandth part of that interval. If the thermometer has been, before the experiment, sufficiently long in the calorimeter to take up its permanent position, and if the rise of temperature is then made to take place, the position of the zero in the final period must lie between its original value and that corresponding to permanent immersion in the final temperature. The error made by either assumption cannot exceed one part in a thousand, and we may form a sufficiently good estimate as to the actual zero value to reduce considerably the limits of possible mistake. But the slow set of the glass envelope which shows itself in the shifting zero, may affect our results in another way. The correction due to loss of heat by radiation and conduction is generally determined by observing the temperature of the calorimeter at the beginning and conclusion of the experiment. But even if there is no loss in the final stage, the thermometer will apparently fall slowly, owing to the imperfect behaviour of the glass envelope. Let the rate of fall be \( \beta \); if the calorimetric observations are conducted in the usual way we should over-estimate that loss by the quantity \( \beta \). If the time during which the calorimeter has been rising in temperature is \( \tau \), we may correct for the error made in this way by adding \( \frac{1}{2} \beta \tau \) to the final temperature, or deducting \( \frac{1}{2} \beta \tau \) from the zero. This is equivalent to saying that we may correct for the set of the glass envelope in a calorimetric measurement by taking for the zero during the final stage the zero shown by the thermometer after immersion in the final temperature during a period equal to half the length of time it has taken the thermometer to rise from its initial to its final value. In our experiments this would be between four and five minutes.

To obtain some clearer information as to time taken by our thermometers to arrive at this permanent zero a series of experiments were carried out. We had a thermometer (Baudin, 12773) which in all respects was as nearly as possible like the one used in our calorimeter experiments (12772). The former was placed in water of about 22°, and kept there for over four hours, the latter was kept during the same time at a temperature of from 10° to 12°, and then suddenly raised to the higher temperature and placed side by side with No. 12773. The two thermometers were read alternately every quarter of a minute for about a quarter of an hour, so as to obtain a good comparison. After the lapse of another hour a similar set of readings were taken at the same temperature. As the mercury threads stand between the same divisions in the two cases, a systematic difference in the reading cannot be due to any calibration errors. The following Table III. gives the results of the comparisons. The times are given in minutes reckoned from the moment that 12772 was placed beside 12773. The column headed \( \Delta \) denotes the difference between the indications of the two thermometers, 12772 always reading higher.
For the present we cannot do better than use thermometers made either of standard Jena or French glass, as their behaviours have been thoroughly studied. By making use of the published investigation, we may then refer our measurements to the thermometers of Berlin or Sèvres.

In calorimetric researches it is often impossible or inadvisable to determine the zero after each measurement. The behaviour of standard glass is so regular that, after the thermometer has been in air for a few years, we may predict with considerable accuracy the position of the zero from a knowledge of the temperature to which the instrument has been exposed. The following Table will illustrate this point.

**Table II.**

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature C.</th>
<th>Zero observed</th>
<th>Observed zero reduced to 760 millims.</th>
<th>Calculated zero.</th>
<th>Difference.</th>
</tr>
</thead>
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<tr>
<td>Dec. 19</td>
<td>12.47</td>
<td>0.0167</td>
<td>0.0194</td>
<td>0.0193</td>
<td>+0.0001</td>
</tr>
<tr>
<td>12</td>
<td>13.25</td>
<td>0.0194</td>
<td>0.0183</td>
<td>0.0183</td>
<td>-0.0010</td>
</tr>
<tr>
<td>12</td>
<td>14.14</td>
<td>0.0162</td>
<td>0.0185</td>
<td>0.0186</td>
<td>-0.0001</td>
</tr>
<tr>
<td>12</td>
<td>22.36</td>
<td>0.0150</td>
<td>0.0187</td>
<td>0.0178</td>
<td>+0.0009</td>
</tr>
<tr>
<td>13</td>
<td>22.45</td>
<td>0.0080</td>
<td>0.0104</td>
<td>0.0102</td>
<td>+0.0002</td>
</tr>
<tr>
<td>13</td>
<td>22.58</td>
<td>0.0086</td>
<td>0.0123</td>
<td>0.0101</td>
<td>+0.0022</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>0.0085</td>
<td>0.0115</td>
<td>0.0100</td>
<td>+0.0015</td>
</tr>
</tbody>
</table>

The second column gives the temperature to which our standard thermometer had been exposed previous to the zero determination; the third column gives the observed zero, measured by an eye-piece micrometer, the fourth place of decimals having no significance; the fourth column gives the observed zero corrected for change due to the varying pressure on the bulb. According to Guillaume, the zero of a thermometer after exposure to a temperature $t$, should be capable of expression in the form $z = 0.00092 \left( t - 15^\circ \right)$ where $z$ is the zero corresponding to the temperature of $15^\circ$. The fifth column gives the zero reading calculated according to this formula, taking for $z$ the value 0.0170; the sixth column shows the difference between the calculated and the observed reduced values.

The agreement is satisfactory, especially for the lower temperatures. The experiment on December 12 was made after exposure of the thermometer to the temperature of $22^\circ$ during four hours, and the zero is seen to be exactly that calculated from the formula. In the two last observations the thermometer had only been kept in the water for about two and a half hours; and we conclude from the observations that the time was not quite sufficient to lower the zero through its full amount.

A little consideration is necessary to decide how far the uncertainty of the zero
DETERMINATION OF THE SPECIFIC HEAT OF WATER.

Table III.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature previous to comparison.</td>
<td>°</td>
<td>10°4</td>
<td>°</td>
<td>°</td>
<td>°</td>
</tr>
<tr>
<td>Temperature during comparison.</td>
<td>21°2</td>
<td>21°2</td>
<td>21°3</td>
<td>21°2</td>
<td>21°2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time.</th>
<th>Δ.</th>
<th>Time.</th>
<th>Δ.</th>
<th>Time.</th>
<th>Δ.</th>
<th>Time.</th>
<th>Δ.</th>
<th>Time.</th>
<th>Δ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.</td>
<td>2:5</td>
<td>0°0128</td>
<td>m.</td>
<td>2:3</td>
<td>0°0108</td>
<td>m.</td>
<td>2°0</td>
<td>0°0137</td>
<td>m.</td>
</tr>
<tr>
<td>h.</td>
<td>6:5</td>
<td>0°0113</td>
<td>h.</td>
<td>5:5</td>
<td>0°0116</td>
<td>h.</td>
<td>6:5</td>
<td>0°0132</td>
<td>h.</td>
</tr>
<tr>
<td>s.</td>
<td>75°0</td>
<td>0°0104</td>
<td>s.</td>
<td>69°0</td>
<td>0°0092</td>
<td>s.</td>
<td>80°0</td>
<td>0°0125</td>
<td>s.</td>
</tr>
</tbody>
</table>

It appears from the table that the thermometer suddenly plunged into water at a temperature of about 10° higher than that to which it was previously exposed, will, during the first hour show a gradual lowering of its indications, corresponding to the lowering of its zero point, amounting to about 0°-0012. Even after the first hour the change will not be complete, as is seen from Table III.; the experiments made on Dec. 13 and 19 showing that after two hours and a half, the zero is still too high by about 0°0018. The first indications of the thermometer must have been too low therefore by about 0°004. As the total change of zero corresponding to the rise from 11°4 to 21°2 is 0°009, it follows that about half the depression takes place in the first few minutes.

In view of these experiments we conclude that the zero of a thermometer of French glass used in calorimetric determinations may after the lapse of a few minutes be assumed to have a position half-way between those corresponding to the lower and the higher temperatures. The extreme uncertainty of this range is less than one part in two thousand, but it is practically certain that an error of more than one part in five thousand cannot be introduced by the assumption made.

Thé Thermometers.

We used as primary standard a thermometer made by Tonnelot (No. 4929). A complete calibration and examination of this instrument was made for us by the "Bureau International des Poids et Mesures" at Paris. The thermometer is divided into tenths of a degree, the length of each degree being 0°58 centim. The divisions are beautifully sharp and can be read both in front and behind the mercury thread. The stem is cylindrical and has a diameter of 0°45 centim. The bulb has a length of 4°8 centims. and a diameter very nearly equal to that of the stem.
A thermometer plunged into a calorimeter can only be read with convenience when the thread is a few inches above the level of the water; and if the length of a degree is short, the correction for the emergent stem becomes serious. It is important that this correction should be small, as it cannot be ascertained with great accuracy. Hence it is better for calorimetric measurements to use a thermometer with an open scale so that nearly the whole thread may be immersed. The open scale has the further advantage of being more easily read. It is generally supposed that the accuracy of thermometer measurements is increased by using a thermometer in which the length of a degree is made very large, and the manufacture of such thermometers has been pushed to ridiculous extremes. Our experience confirms the conclusion drawn by Guillaume ("Thermométrie," p. 180), that the uncertainties in the indications of a thermometer measured in degrees increase with an increase in the length of the degree, and that, therefore, apart from the convenience of reading, the advantage altogether is in favour of a short degree. When the whole thermometer can be plunged in water and the temperature of the water is kept sufficiently steady to allow a careful reading, a thermometer such as that of Tonnelot, divided into tenths of a degree, the divisions being half a millimetre apart, allows as accurate a determination of temperature as any mercury thermometer can give us at present.

It was the uncertainty of the correction of the emergent stem which finally decided us to use in our calorimeter a thermometer with an open scale; but it was essential that it should be made of the same glass as the standard. We chose one by Baudin (No. 12772), having a length of degree of 3·1 centims. approximately, and being divided into fiftieths. It contained according to the statement of the maker 33·0 grams of mercury. It could be read at the freezing-point and between 12° and 23°. The stem was shortened by an expansion in the glass above the zero point in such a way that the distance from the division which marked 12° to the centre of the main bulb was only 8·1 centims. The radius of the bore can be calculated from the weight of mercury, and is thus found to be 0·0061 centim. From experiments made under varying pressures, the thickness of the glass bulb can be roughly estimated as 0·066 centim. In order to allow us to use the thermometer for our purpose it was necessary (1) to calibrate the thermometer, (2) to compare it with the standard, (3) to determine carefully the pressure coefficient, as the comparison had to be conducted with the thermometer in a horizontal position.

The Calibration.

The calibration was conducted according to the method of Thiessen, as described by Guillaume. Threads were broken off, having a length of very nearly one, two, &c., up to ten degrees, and these threads were pushed forward from degree to degree. Their lengths were measured on the thermometer in the usual way, an estimate of the overlapping of the mercury to one-hundredth part of a division being made by the eye,
looking through a telescope of small magnifying power, but without a micrometer. The observations with every thread were repeated more than once, often by different observers. The final result is given in Table IV., in which the second column gives the calibration correction in thousandth parts of one division. The reductions are easily made by the method of least squares in the manner indicated by Thiessen. The probable error of a single observation* was calculated to be 0.020 division, and the probable error in the final correction at each point is 0.008 division, or, as the thermometer was divided into fiftieths, the probable error in the calibration correction is 0°.00016.

**Table IV.**

<table>
<thead>
<tr>
<th>Degrees</th>
<th>Calibration correction of the complete series, the unit being 0.001 division = 0°.00002.</th>
<th>Calibration correction deduced from observations made with one thread and eye estimate. 1892.</th>
<th>Calibration correction deduced from observations with one thread and micrometer measurements. 1894.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>13</td>
<td>77</td>
<td>88</td>
<td>75</td>
</tr>
<tr>
<td>14</td>
<td>184</td>
<td>186</td>
<td>172</td>
</tr>
<tr>
<td>15</td>
<td>22</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>16</td>
<td>272</td>
<td>283</td>
<td>246</td>
</tr>
<tr>
<td>17</td>
<td>253</td>
<td>263</td>
<td>257</td>
</tr>
<tr>
<td>18</td>
<td>45</td>
<td>41</td>
<td>38</td>
</tr>
<tr>
<td>19</td>
<td>83</td>
<td>82</td>
<td>122</td>
</tr>
<tr>
<td>20</td>
<td>291</td>
<td>286</td>
<td>314</td>
</tr>
<tr>
<td>21</td>
<td>75</td>
<td>86</td>
<td>50</td>
</tr>
<tr>
<td>22</td>
<td>80</td>
<td>103</td>
<td>88</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

We conclude from this that it is extremely unlikely that our calibration is wrong by 0°.0008 at any point. In order to see how far the eye without micrometer may be trusted to carry out a calibration by means of one thread (Gay-Lussac's method), we give in the third column of Table IV. the calibration corrections deduced from the observations of the thread of one degree. At the conclusion of our experiments it seemed more satisfactory to make certain that no appreciable change had taken place in the thermometer. The calibrations were, therefore, repeated, but this time only with one thread, according to Gay-Lussac's method, and the readings were taken with a micrometer. The results are given in the fourth column. The greatest difference between the corrections found in 1892 and 1894 amounts to about 0.04 division, or 0°.0008; the average difference amounts to less than half that value.

The observations made at the conclusion of our experiments were only intended as a check, and we feel justified in concluding that no change has taken place in the

* By a single observation here is meant the measurement of the mercury thread in one of its positions. Several measurements in the same position are taken, and their mean value counts in the reduction as one observation.

MDCCXCIV. — A.
thermometer, and that our calibration in 1892 was satisfactory. The numbers obtained from the single thread by Gay-Lussac’s method are practically identical with those obtained by the more complete method.

The temperatures for which the corrections have been obtained being too far apart to allow us to interpolate safely for the intermediate points, a thread of 2°.5 was broken off, and by means of it the corrections for every half-degree could be deduced. The divisions of the thermometer were not equidistant, but the maker had attempted to correct for inequality of bore. This method, much in use at one time, causes a good deal of unnecessary labour, as already pointed out by Guillaume, whenever the instrument is to be used for accurate work; its subsequent calibration cannot be dispensed with, and the lengths of the divisions must be measured one by one, as there is no clue where a sudden change in the length may occur. We give in an appendix the method adopted to deduce the final corrections for each division of the thermometer.

Pressure Corrections.

The reservoir of a thermometer is generally subjected to an internal pressure due to the column of mercury forming the thread, and this pressure causes quite an appreciable increase in volume. If the thermometer is always used in the vertical position, no error is caused in assuming uniformity of bore; the effect of internal pressure will only be a shortening of the distance between the fundamental points. Even in this case, however, care must be taken that the range for which the thermometer is used does not include bulbs like those which are placed above the freezing point in calorimetric thermometers.

A comparison between two thermometers is more easily conducted in a horizontal than in a vertical position; and in that case, of course, the effect of pressure must be taken account of.

The effects of external pressure are easily measured by suspending the thermometer in a vessel in which the pressure can be quickly changed from the atmospheric pressure to one of a few centimetres only.

We have used a method which is a slight modification of that given in Guillaume’s book. It is unnecessary to enter into long details, as the method will be described in another communication. Three experiments were made on March 21, 1892. The change of pressure was a sudden diminution from the atmospheric pressure to one of 27 centims. The observations, when reduced, give

\[
\begin{align*}
0.002088 \\
0.002085 \\
0.002080
\end{align*}
\]

Mean \(0.002084\)

as the effect due to 1 centim. of mercury at 0° C. at the latitude of Manchester.
The experiments were repeated two years later, on February 22, 1894, when two different determinations gave

\[
\begin{align*}
0.002096 \\
0.002072
\end{align*}
\]

\[
\text{Mean} \quad 0.002084
\]

It is seen that the changes in atmospheric pressure, which may amount to several centimetres, may produce a change in the indications of a delicate thermometer which cannot be neglected.

From the effect of external pressure we may easily deduce that of internal pressure. If \( P \alpha \) is the diminution of volume due to an increase of pressure \( P \) applied externally, and \( P \beta \) the increase in volume of the same pressure is applied internally, then the diminution in volume due to a simultaneous increase of pressure \( P \) inside and outside is \( P(\alpha - \beta) \), and this must also be equal to \( P/\kappa \), where \( \kappa \) is the compressibility of the walls of the thermometer bulb. Hence

\[
\alpha - \beta = \frac{1}{\kappa}.*
\]

The reading apparently is diminished when the thermometer is raised from the horizontal to the vertical position, not only because the glass bulb expands, but also because the mercury is compressed. If \( \kappa' \) is the resistance to compression of mercury, a pressure \( P \) will have the same effect as an increase of volume \( P/\kappa' \) of the reservoir. Hence, if \( \beta \) now denotes the complete effect of unit increase of pressure applied internally on the reading in degrees of the thermometer, we obtain

\[
\beta = \alpha + \frac{1}{\kappa'} - \frac{1}{\kappa}.
\]

\[
\frac{1}{\kappa'} - \frac{1}{\kappa}
\]

is the relative compressibility of mercury and glass, which is known.

Amagat, whose measurements doubtless are the most accurate at our disposal, finds for glass of medium hardness the relative compressibility to be \( 1.707 \times 10^{-6} \), and for lead glass (cristal) \( 1.512 \times 10^{-6} \) (‘Annales de Chimie et de Physique,’ vol. 22, 1891). For the French thermometer glass the coefficient will not differ much from the larger of these values.

The numbers given refer to the atmosphere as unit pressure. It is more convenient

* This relation is quite general and independent of the shape of the bulb, which need not be of the same thickness throughout, provided it is of homogeneous material. The relation in Guillaume’s book is proved in an elaborate manner for spheres and cylinders, and is then said to hold “no doubt only approximately” for thermometer bulbs.

[Since the above was written, Mr. Chree has published a paper (‘Phil. Mag.’, October, 1894), in which a proof of the relation between the internal and external pressure coefficients practically identical with the above has been given.—June, 1895.]
for our purpose to take as unit pressure that due to a column of mercury 1 centim. long, and for unit change of volume that corresponding to an increase in temperature of one degree. The relative coefficient of thermal expansion of glass and mercury between 10° and 20° C. being $1.598 \times 10^{-4}$, the apparent compressibility of mercury reduced to the new units will be found by dividing the above number, by $76 \times 1.598 \times 10^{-4}$. The relation between $\beta$ and $\alpha$ then becomes

$$\beta = \alpha + 0.000141.$$  

The number used by the Bureau International des Poids et Mesures, founded on some older determinations, is 0.000154, and the uncertainty of this term might be raised as an objection to the use of a thermometer in the horizontal position. But the whole term being of little importance, it does not matter much which of the different possible values we adopt. Thus the difference between Guillaume's internal pressure correction and ours would produce a difference in the measured temperature range of our Baudin thermometer of one part in 25,000, and in the Tonnelot standard it would be equal to only the sixth part of that value. For the sake of uniformity we have continued to use Guillaume's number, and therefore take for the Baudin 12,772,

$$\alpha = 0.002084$$

$$\beta = 0.002238,$$

where $\alpha$ and $\beta$ measure in degrees the changes in the apparent temperature due to a change of pressure of 1 centim. of mercury applied to the outside or inside respectively.

A small correction was necessary to allow for the fact that the mercury in that part of the stem which is not immersed in the calorimeter is not necessarily at the same temperature as the water. To ascertain this correction two small thermometers were used, one placed in the space between the calorimeter and the disc (D, fig. 5) which covered the water jacket, while the other was placed above this disc about half-way between it and the upper end of the thread. We found that in the last period when the calorimeter had risen about 2°, that part of thread below the disc D could be assumed to be at a temperature 1° above that of the air, while that part of the thread which was above the disc had not appreciably changed its temperature. The correction was always small, as the whole rise was only 2° and only a few degrees of the stem were exposed to the air.

The thermometer was always read by means of a cathetometer telescope, the cathetometer stand being very convenient to move the telescope parallel to itself. The avoidance of parallax is of importance and can be easily secured in this way, provided the thread is always read when in the middle of the field.
Comparison of Thermometers.

Having found the calibration correction of a thermometer, it remains to determine its range. The calibration of our calorimetric thermometer was carried out between the points marked 12° and 23° respectively, and in order to find the interval between those points according to some fixed scale, it would seem most natural to compare the thermometer near the extreme points of its range with a standard. This we attempted to do at first, but found that the results of different comparisons were not as concordant as we could have wished. Two thermometers, however, carefully calibrated, will show differences when compared with each other amounting to a few thousandths of a degree, and there seems little doubt that local irregularities, either in the width of the bore, or in the nature of the surface affecting the capillary constant, render the readings of a mercury thermometer uncertain to that extent. These irregularities are more likely to occur near the ends of the scale where the tube had to be blown out into a bulb or joined to the reservoir. We decided therefore to compare the Baudin and Tonnelot along the whole scale in order to obtain as accurate a value for the Baudin as possible.

The comparisons were carried out in a horizontal bath with a slowly rising temperature. It is unnecessary here to enter into the details of the construction of the apparatus and method of comparison, as these will be furnished in another communication. Table V. shows the result. Column II. gives the reading $T_B$ of the Baudin thermometer, corrected for calibration and division errors and reduced to the vertical position. The third column gives the correction $\gamma$ which has to be applied to the Baudin thermometer in order to reduce it to the readings of the standard mercury thermometer made of French glass. The values of $\gamma$ are those obtained by experiment. Calling $t_B$ the reading of the Baudin thermometer, we require to express $\gamma$ as a linear function of the temperature in the form

$$\gamma = \alpha + bT_B.$$ 

Reducing the observations by the method of least squares, we found

$$\alpha = + 0.0194$$
$$b = - 0.00089 \pm 0.000047.$$ 

Calling $\gamma'$ the value of $\gamma$ calculated with the help of these data, $\gamma' - \gamma = \Delta$ will express the difference between the calculated and observed corrections to the Baudin thermometer. The fourth column of the table in which $\Delta$ is entered shows that the agreement is satisfactory. The residual differences are accounted for by errors of observation, by remaining errors of calibration of the two thermometers and by irregularities in the capillary phenomena. The probable error of a single comparison is found to be $0.000096$, that is about one thousandth of a degree, and the probable error of the interval is about one part in 20,000.
In the comparison of the calorimetric and standard thermometers, the two were always treated exactly in the same manner, and exposed simultaneously to the same temperatures; hence we may assume that their zeros varied equally, and, as the zero of the standard was assumed that corresponding to the steady state of the thermometer after it has been exposed for a sufficiently long time to the temperature of comparison, the correction found for the Baudin applies to the ultimate reading of that thermometer at any temperature. As it has been shown that we must in our experiments take the zero to be halfway between its initial and final positions, the

| Table V. |  |
|---|---|---|---|
| I. | II. | III. | IV. |
| Comparison. | $T_p.$ | $\gamma.$ | $\Delta.$ |
| 1 | 12.585 | +0.0072 | +0.0010 |
| 2 | 12.643 | +0.0068 | +0.0014 |
| 3 | 12.885 | +0.0073 | +0.0006 |
| 4 | 12.923 | +0.0051 | +0.0028 |
| 5 | 13.068 | +0.0068 | +0.0010 |
| 6 | 13.315 | +0.0080 | -0.0014 |
| 7 | 13.393 | +0.0088 | -0.0013 |
| 8 | 13.687 | +0.0071 | +0.0001 |
| 9 | 14.023 | +0.0075 | -0.0006 |
| 10 | 14.103 | +0.0096 | -0.0027 |
| 11 | 14.171 | +0.0074 | -0.0006 |
| 12 | 14.184 | +0.0075 | -0.0007 |
| 13 | 14.580 | +0.0067 | -0.0003 |
| 14 | 15.132 | +0.0076 | -0.0017 |
| 15 | 15.194 | +0.0065 | -0.0006 |
| 16 | 15.538 | +0.0052 | +0.0004 |
| 17 | 15.881 | +0.0057 | -0.0005 |
| 18 | 16.018 | +0.0035 | +0.0012 |
| 19 | 16.534 | +0.0037 | +0.0010 |
| 20 | 17.226 | +0.0062 | -0.0021 |
| 21 | 17.322 | +0.0037 | +0.0030 |
| 22 | 17.964 | +0.0035 | -0.0001 |
| 23 | 17.997 | -0.0005 | +0.0039 |
| 24 | 18.032 | +0.0026 | +0.0008 |
| 25 | 18.383 | +0.0032 | -0.0003 |
| 26 | 18.999 | +0.0026 | -0.0001 |
| 27 | 19.107 | +0.0023 | +0.0001 |
| 28 | 19.464 | +0.0015 | +0.0006 |
| 29 | 19.997 | +0.0041 | -0.0025 |
| 30 | 20.011 | +0.0006 | +0.0010 |
| 31 | 20.055 | +0.0021 | -0.0005 |
| 32 | 20.545 | +0.0006 | +0.0005 |
| 33 | 21.065 | +0.0028 | -0.0021 |
| 34 | 21.103 | +0.0005 | +0.0001 |
| 35 | 21.485 | +0.0006 | -0.0003 |
| 36 | 21.501 | +0.0008 | -0.0005 |
| 37 | 22.054 | +0.0004 | -0.0006 |
| 38 | 22.145 | -0.0096 | +0.0033 |
| 39 | 22.451 | -0.0010 | +0.0004 |
| 40 | 22.831 | -0.0011 | +0.0002 |
corrections under the condition of our experiments have to be diminished by 0.00046; hence, if \( t \) is any interval of temperature on the standard thermometer, and \( t_B \) that on the Baudin thermometer, we find finally

\[
t = t_B (1 - 0.00135).
\]

We have made a few observations which check the correction (0.00046) we have made to eliminate the error due to the fact that, in the actual equivalent experiment, the zero of our Baudin had not reached its final state. The Baudin was placed in water at a temperature 10° above that at which it had previously been kept, and was compared after the lapse of about ten minutes with the standard. The latter instrument had been immersed in the warm water for several hours, and its zero was determined at the conclusion of the comparison. The corrections thus found on three different days for the Baudin were \(-0.0059\), \(-0.0069\), \(-0.0053\), or \(-0.0060\) in the average, at a mean temperature of 22°6. Taking the correction at 12° to be that found above, viz., 0°0082, we should get an interval correction of \(-0.00142\), holding for the conditions of the experiment closely resembling those of the equivalent experiments. The difference between this number and the one adopted \((-0.00135\) is less than one part in a thousand.

The Calorimeter and Water-equalities.

The calorimeter consisted of a copper vessel, heavily gilt outside and inside, the weight of gold deposited being about 1.6 grms. The copper vessel was of the usual cylindrical form, and had the following dimensions:—

- Height: 17.9 centims.
- Diameter of section: 11.0 cm.
- Thickness of walls: 0.0295 centim.
- Total weight of calorimeter: 161.3 grms.

The following data will show the agreement between different determinations of the specific heat of copper:

<table>
<thead>
<tr>
<th>Observer</th>
<th>Specific heat</th>
<th>Range of temperature through which copper was cooled</th>
<th>Mean temperature of copper</th>
<th>Temperature of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regnault (Naccari)*</td>
<td>0.0933</td>
<td>100 - 17</td>
<td>59</td>
<td>17</td>
</tr>
<tr>
<td>Tomlinson</td>
<td>0.0938</td>
<td>100 - 20</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>Bêde</td>
<td>0.0933</td>
<td>100 - 15</td>
<td>58</td>
<td>20</td>
</tr>
<tr>
<td>Joule</td>
<td>0.0921</td>
<td>40 - 8</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>Tomlinson</td>
<td>0.0926</td>
<td>60 - 20</td>
<td>40</td>
<td>20</td>
</tr>
</tbody>
</table>

* Regnault gives a higher value, based apparently on a wrongly-assumed value of the specific heat of lead. The above value is that which Naccari has recalculated from Regnault's observations, correcting for the error.
The mean of the first set of three observations gives '0935 for the specific heat of copper at 59°, and the mean of the last two '0924 for the specific heat at 32°. The average temperature at which our observations were made was 19°, and, assuming the specific heat to be a linear function, we may with sufficient accuracy adopt for its value '0918. The water-equivalent of the calorimeter, taking account of the small quantity of gold on it, is thus found to be 14.71. An error of 1 per cent. in this value would change our result by one part in ten thousand, and we may certainly trust the assumed specific heat of copper to that degree of accuracy. Our heating coil and frame were made of brass, porcelain, glass, platinoid, and shellac. After the conclusion of our experiments the whole of the heating frame, coil, and stirrer was broken up and enclosed in a cage of copper gauze, and its water-equivalent determined, with the following result:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Water equivalent</th>
<th>Mean temperature of copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.62</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>9.72</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>9.68</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>9.96</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>9.95</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>9.98</td>
<td>58</td>
</tr>
</tbody>
</table>

From these figures we calculate the water-equivalent at 19° to be 9.59.

We had originally intended to calculate the water-equivalent of our frame and coil by adding the equivalents of its parts, and we had for this purpose made some experiments on the specific heat of porcelain and platinoid. The experiments were not quite satisfactory, in the first place, because they related to a temperature higher than the one used in our experiments, and secondly because when they were made we had not quite realised what serious errors may be introduced, even with the best thermometers when the temperature during the last period is falling. Our values, for this reason, were no doubt too high. Although we trust entirely to the water-equivalent 9.59, which was directly determined with all precautions, and with a thermometer rising during the whole course of the experiments, we nevertheless give as a check the equivalents calculated from that of its parts.
This refers to a temperature of about 60°, and agrees sufficiently well with the equivalent 9·96 which was directly determined, if we remember that the specific heats of porcelain and platinoid are, for the reasons given, too high, and that the values for the specific heat of brass and glass were assumed to be those usually given.

We must add 0·34 to the water-equivalent belonging to a silver disc covered with gold foil, which was kept floating on the surface of the water in order to prevent evaporation as far as possible.

As regards the thermometer, we calculated the specific heat from the data inscribed on it by the maker, according to which the weights were as follows:

| Weight of mercury | 33 grams. |
| Weight of glass bulb | 1·83 grams. |
| Weight of glass in stem | 25·79 |

Taking the specific heat of mercury to be 0·033, and that of glass 0·19, we calculate that the water-equivalent up to the point marked 12° was 2·05. An experiment made to determine directly the equivalent of the thermometer, showed that we could trust the figures given by the maker, the value found being identical with that calculated from his data. We may add 2·05 permanently to the water-equivalents, and in the separate experiments correct for the additional length of the stem immersed, which was slightly different on different occasions. The correction is determined by the fact that the water-equivalent corresponding to a length of 1° of the stem is 0·34. We may take, therefore, as the equivalents which were the same in all experiments:

| Calorimeter | 14·71 |
| Heating coil, frame and stirrer | 9·59 |
| Silver disc | 0·34 |
| Thermometer as far as mark 12° | 2·05 |
| Parts surrounding calorimeter | 0·33 |

\[ \text{Total} = 27·02 \]
The reason for the last item will be given in connexion with the discussion of the cooling correction.

The Total Mass of Water.

The calorimeter contained approximately 1514 grams of distilled water in each experiment. The mass of water was determined by volume and by weight. In the estimation by volume a carefully calibrated 500 cub. centims. flask and burette were used. The weighings were taken on a balance, allowing, to estimate accurately, 0.1 gram. The buoyancy correction amounts to 1.58 gram.

As our calorimeter was not completely covered, a certain amount of evaporation took place, the mass of water during the experiment differing by about a decigram from that which was put in. A few experiments give a fairly consistent rate of 0.11 gram per hour of evaporation under the conditions of our experiment. As a check the water was nearly always weighed both before and after each experiment, and the mass during the experiment was then found by interpolation.

The Cooling Correction.

The interchange of heat between the calorimeter and its surroundings depends on conduction and radiation. If the water of the calorimeter is exposed to the air, evaporation may sensibly lower the temperature, but for the present we may disregard the effects of evaporation. The loss of heat to the outside is usually corrected for in a well-known manner. The correction depends on the assumption that the loss of heat is proportional to the difference in temperature between the calorimeter and its enclosure, and if the loss of heat is small, the assumption is generally justified. In a well-disposed experiment the temperature (u) of the calorimeter alters slowly and regularly during the preliminary period. If n observations are made at regular intervals of time T, they should be expressible with sufficient accuracy in an expression of the form \( u = v + kT \). It is usual to obtain the two constants of this equation \( v \) and \( k \) by graphical means; we have employed instead the method of least squares, not for the reason that we believe to have obtained a greater degree of accuracy in this way, but simply as a matter of convenience. The process of calculation takes less time than the graphical method, and the results are quite free from personal bias. The observations themselves give a series of equations,

\[
\begin{align*}
  u_1 &= v + kT \\
  u_2 &= v + 2kT \\
  &\vdots \\
  u_n &= v + nkT.
\end{align*}
\]

It is required in the first place to calculate \( v \) and \( k \). The most probable values of \( v \) and \( k \) are
\[
\frac{1}{2} n (n - 1) v = (2n + 1) A - 3B
\]
\[
\frac{1}{2} n (n - 1) (n + 1) kT = 2B - (n + 1) A,
\]
where
\[
A = u_1 + u_2 + \ldots + u_n
\]
\[
B = u_1 + 2u_2 + \ldots + nu_n.
\]

The last observation being taken, the second period—in which the heat to be measured is allowed to enter the calorimeter—begins after a further interval \( T \), and it is required to calculate, in addition to the rate of heating \( kT \), the most probable value \( u_{n+1} \) of the temperature at the beginning of the second period. The above equations give
\[
u_{n+1} = v + (n + 1) kT
\]
\[
= \frac{6B - 2(n + 2) A}{n(n - 1)}.
\]

In our case, where the rise in temperature was always small and regular, ten or twelve observations were considered sufficient to determine the constants, and in that case the labour of reduction is small.

After an experiment the change in temperature of the calorimeter had to be observed once more, and a value \( k' \) corresponding to \( k \) was again determined in a similar manner. From the two values \( k \) and \( k' \) the loss of heat of the calorimeter during the whole of the experiment could easily be calculated, for the rise in temperature during the actual heating was uniform. If the current passed during \( m \) intervals, each equal to \( T \), and if \( -k \) and \( -k' \) denote the rates of cooling during the first and last periods, the loss of heat during the \( m \) intervals was \( \frac{1}{2} m (k + k') \). A small correction was necessary owing to the fact that the observed values of \( k \) and \( k' \) did not correspond to the temperature of the calorimeter at the beginning and end of the second period.

We have now to examine shortly how far errors in the estimation of the cooling correction may arise. Newton's law of cooling is known to be approximate only. If we had to deal simply with radiation, we should obtain greater accuracy by adopting the law of Stefan, according to which radiation varies as the fourth power of the absolute temperature. We have calculated that the difference introduced by Stefan's law in the final value of the equivalent amounts to about one part in sixty thousand, and considering that the combined effect of radiation and conduction seems to follow Newton's law more closely than the effect of radiation alone, we are justified in taking that law as correct. In order that the usual cooling correction should apply, it is not necessary that the different parts of the enclosure should all be at the same temperature, nor is it always necessary that the temperature of the surrounding bodies should be constant. If, as in our case, the calorimeter receives its heat at a constant rate, the temperature of the enclosure may vary as a linear function of the
time during the same time without vitiating the experiment, for as long as we assume Newton's law, it does not matter whether the calorimeter rises uniformly or the enclosure falls uniformly or whether they both vary together. This is an important consideration, for unless we take very elaborate precautions, the enclosure must to a certain extent follow the temperature of the calorimeter. All that is requisite for a correct estimate of the cooling is that the rates should be accurately known at the beginning and ending of the second period. The change in temperature of our water jacket in the actual experiments was very small and sometimes inappreciable.

When the temperature of our calorimeter was raised 1° above that of the water jacket, the cooling amounted to about 0°0025 per minute; the cooling surface was about 725 sq. centims.; the amount of water in the calorimeter, 1,500 grams. Hence there was a loss of heat for each square centimetre of surface of 0·0052 unit per minute. In Mr. E. H. Griffiths' determination, where the pressure of the surrounding space was reduced to about one-hundredth atmosphere, the corresponding number was between 0·0028 and 0·0026, taking 300 sq. centims. as the exposed surface. On the other hand, his total amount of water was always less than one-quarter of that used by us; so that the actual cooling in his experiments for one degree difference was about double ours. It is interesting also to compare our number with that corresponding to the loss from a cylindrical rod suspended horizontally in the air and quite unprotected. Mr. Lees (Phil. Trans., Vol. 183, p. 490) finds for a nickel-plated rod of about 2 centim. diameter, 0·011 gramme-degree per square centimetre per minute, or about twice our number. In the latter case, the conditions of the experiment are most favourable for great loss of heat by convection; and Mr. Griffiths' experiments show that by reduction of pressure to about one-third of a millimetre the loss is only reduced to about one-quarter of what it is in that case, and one-half of what it may easily be reduced to in a calorimetric experiment at atmospheric pressure. It ought to be possible by properly disposed diaphragms to reduce considerably the effects of convection currents at atmospheric pressure and so gain in a simple way the same advantage as is done by removing the air surrounding the calorimeter.

We may calculate approximately that part of the loss which is due to conduction irrespective of convection. Taking the thermal conductivity of air to be 0·000055, and the distance between the calorimeter and the enclosure as 3·8 centims., we find that thermal conductivity alone would account for a loss of roughly 0·001 gramme-degree, or about one-fifth only of the actual loss. As in Mr. Griffiths' experiments the enclosure was at a greater distance from his calorimeter than ours, his observed loss by radiation and conduction is also about five times that due to conduction of air alone.

Evaporation will produce a certain amount of cooling of the calorimeter, if that is not perfectly enclosed; but unless the rate of evaporation changes with the temperature, the effect will only be a lowering of temperature by a constant quantity.
The rate of cooling can only be affected by evaporation in so far as it increases with the temperature, and since for small changes it would vary as a linear function of the temperature, any error due to evaporation is eliminated by the cooling correction.

*Some Corrections to the Water-equivalents.*

1. **Correction for Surrouning Air.**—The usual method of finding the value of the correction depends on the assumption that the loss of heat is proportional to the excess of temperature, and as regards radiation this will hold whenever the variation is small. When however an appreciable quantity of heat is carried away by conduction, an error may be introduced by taking as the excess of temperature the difference observed between that inside the calorimeter and that of its jacket, for the temperature gradient in that case will not be uniform during the whole course of the experiment. Consider, for instance, a calorimeter placed on a more or less conducting material like wood or cork. If the calorimeter is suddenly heated, the temperature gradient at the surface will be large and will then slowly diminish. The cooling observed, as usual, after the lapse of a few minutes, will underrate the heat lost during the first few minutes. It is easy to see that when conduction comes into play, the amount of heat lost or gained will depend on the distribution of heat in the conducting body, and that will depend on the previous history of the calorimeter. Thus, when a calorimeter is kept heated until all the surrounding parts have reached a steady temperature, and observations are then made on the rate of cooling, we are not justified in applying the rate thus formed to the period in which heat is communicated to the calorimeter. An estimate may be made of the error introduced if the correction is applied in the usual way. We take the case of a calorimeter placed on a non-conducting slab of thickness $c$. At the beginning of the experiment everything is to be at temperature zero. At the time $t = 0$, the temperature ($u$) of the calorimeter is to be gradually and uniformly raised so that we may take $u = pt$. Finally, at a time $T$, the temperature is kept constant and equal to $pT$. It is required to find the rate at which heat is given up by the calorimeter at any moment, and the total amount of heat which passed through its surface.

Taking the flow to be linear, the differential equation to be satisfied is

$$\frac{\partial u}{\partial t} = \alpha^2 \frac{\partial^2 u}{\partial x^2}.$$ 

Here $\alpha^2 = \kappa/s$, where $\kappa$ represents the conductivity and $s$ the heat capacity per unit volume. We introduce the conditions

$$u = 0 \text{ if } t = 0 \text{ for all values of } x,$$

$$u = \phi(t) \text{ for } x = 0,$$

$$u = 0 \text{ for } x = c \text{ for all values of } t.$$
Also \( \phi(t) = pt \) between \( t = 0 \) and \( t = T \), and \( \phi(t) = pT \) if \( t > T \).

The solution of the differential equation can be put into the form

\[
u = \phi(t) \left\{ \frac{e^{-\frac{x}{c}} - \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi}{c} x}{e} \right\} + \frac{2\beta^2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \int_{0}^{t} e^{-\frac{\nu^2(t-\lambda)}{c^2}} \phi(\lambda) \, d\lambda,
\]

where \( \beta \) is written for \( \alpha \pi/c \).

The first term is often omitted as it vanishes for all finite values of \( x \). But as we shall have to consider the value of \( \partial u/\partial x \) for \( x = 0 \), it is retained here. To perform the integration we must distinguish two cases, according as \( t \) is smaller or greater than \( T \). Taking \( \phi(\lambda) = \rho \lambda \), and performing the integration with respect to \( \lambda \), we find

\[
u = pt \left\{ \frac{e^{-\frac{x}{c}}}{e} - \frac{2\rho}{\pi\beta^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left( 1 - e^{-\frac{\nu^2t}{c^2}} \right) \sin \frac{n\pi x}{c} \right\} \ldots \ldots \quad (1)
\]

for \( t < T \).

For larger values of \( t \) we have to divide the integral into two parts as the value of \( \phi(\lambda) \) has a discontinuity for \( t = T \).

The final equation for \( u \) then becomes

\[
u = pT \left\{ \frac{e^{-\frac{x}{c}}}{e} - \frac{2\rho}{\pi\beta^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{\nu^2t}{c^2}} \right\} \sin \frac{n\pi x}{c}.
\]

Writing \( (\partial u/\partial x)_0 \) for the value of \( \partial u/\partial x \) at the plane \( x = 0 \), the quantity of heat passing out of the calorimeter up to the time \( T \) will depend on

\[
-\int_{0}^{T} (\partial u/\partial x)_0 \, dt = \frac{1}{e} \int_{0}^{T} \left\{ pT + 2p \sum_{n=1}^{\infty} \frac{1}{n^2 \beta^2} \left( 1 - e^{-\frac{\nu^2t}{c^2}} \right) \right\} dt
\]

\[
= \frac{pT^2}{2c} + \frac{p \nu^2 T^2}{3 \alpha^2} - \frac{p \nu^2}{45 \alpha^4} + \frac{2 \nu^2}{\pi^2 \alpha^4} \sum_{n=1}^{\infty} \frac{1}{n^4} e^{-\frac{\nu^2t}{c^2}}.
\]

We also obtain if \( t > T \)

\[
-\int_{0}^{t} (\partial u/\partial x)_0 \, dt = \frac{pT}{2c} (2t - T) + \frac{p \nu^2 T}{3 \alpha^2} + \frac{2 \nu^2}{\pi^2 \alpha^4} \sum_{n=1}^{\infty} \frac{1}{n^4} e^{-\frac{\nu^2t}{c^2}} (1 - e^{-\frac{\nu^2T}{c^2}}).
\]

The application of these formulas is easy when \( \beta^2 t \) is so large that \( e^{-\frac{\nu^2t}{c^2}} \) may be neglected. The heat \( H \) which has passed through unit surface of the calorimeter up to the time \( t \) is obtained by multiplying the right-hand side of the last equation by \( k = \alpha^2 s \).

Neglecting the last term this becomes

\[
H = \frac{pT}{2c} (2t - T) + \frac{p \nu^2 T}{3 \alpha^2}.
\]
and the rate at which heat is given up at the time \( t \) is

\[
d\mathcal{H}/dt = \frac{pkT}{c}.
\]

If the cooling correction is applied in the usual way, the rate at which heat is lost would, during the period of heating, be taken as half that corresponding to the final period, or in other words we should take loss of heat as \( \frac{pkT}{2c} \) during the period of heating, and as \( \frac{pkT}{c} (t - T) \) from the time that the temperature of the calorimeter has become steady. It is seen that in this way of calculating, the term \( \frac{1}{3} (\rho c s t) \) is neglected. This term represents the amount of heat which is necessary to raise a thickness \( \frac{1}{3} \) of the material through which the heat is conducted to the final temperature of the calorimeter.

We see from this investigation that a certain amount of the air surrounding the calorimeter should be added to the water-equivalent. For air \( a^2 \) is about 0.26, and in our experiments the walls of the enclosure were 3.8 centims. from the calorimeter. We may, without sensible error, neglect the error due to the curvature of the sides of the calorimeter and substitute 3.8 for \( c \). The value of \( \beta^2 \) then becomes

\[
0.26\pi^2/ (3.8)^2 = 0.18.
\]

As several minutes always intervened between the time at which the temperature of the calorimeter had become constant and the observations for the cooling correction, \( \beta^2 (t - T) \) was always greater than 10 and \( e^{-\beta^2 (t - T)} \) was therefore quite negligible. We may in this case then simply calculate the water-equivalent of a quantity of air surrounding the calorimeter, and having a thickness of \( c/3 \) or 1.3 centims. The total effective surface of the calorimeter being 724 sq. centims., the quantity to be added to the water-equivalent becomes 0.28.

2. Correction for Thermometer.—In taking the water-equivalent of the thermometer, it is usual to consider only that part which is plunged into the water, but this requires justification, as it is clear that those parts of the thermometer which are close to, but not actually in contact with the water, must be heated also. The following calculation will give an estimate of the error which may be thus introduced. We may assume, in the first instance, that the thermometer which is surrounded by air rising from the calorimeter will not give up any appreciable heat to the outside, so that we may apply the same differential equation for the flow of heat as that used in the former problem. We may treat the thermometer as a glass rod of indefinite extent, having the temperature of its surface in contact with the water raised at a uniform rate \( pt \) until \( t = T \) when it is kept constant at the temperature \( pT \).

The solution of the equation applied to this case gives us :—
\[-\left(\frac{\partial u}{\partial x}\right)_0 = \frac{2p}{a\sqrt{\pi}} \sqrt{t} \text{ for } t < T\]
\[-\left(\frac{\partial u}{\partial x}\right)_0 = \frac{2p}{a\sqrt{\pi}} (\sqrt{t} - \sqrt{t - T}) \text{ for } t > T\]
\[- \int_0^t \left(\frac{\partial u}{\partial x}\right)_0 dt = \frac{4}{3} \frac{pT^{3/2}}{a\sqrt{\pi}}\]
\[- \int_0^t \left(\frac{\partial u}{\partial x}\right)_0 dt = \frac{4}{3} \frac{p}{a\sqrt{\pi}} (\sqrt{i^3} - \sqrt{(i - T)^3}).\]

In our experiments the average time \(t\) during which the rate of cooling was observed was with sufficient accuracy equal to \(2T\), reckoned from the moment the heating began. In that case, the above formulae show that the total amount of heat which has passed into the thermometer, denoting by \(A\) the area of its cross-section, is

\[\frac{4\kappa\rho T^{3/2}}{3a\sqrt{\pi}} \left[2\sqrt{2} - 1\right];\]

while the heat lost to the calorimeter, calculated by means of the cooling during the last period, is

\[\frac{3\kappa\rho T^{3/2}}{a\sqrt{\pi}} \left[2\sqrt{2} - 1\right].\]

The quantity to be added to the water-equivalent is obtained by dividing the difference of these values by \(\rho T\), and becomes therefore

\[\frac{\kappa A}{3a} \sqrt{\frac{T}{\pi}} \left(5 - \sqrt{2}\right) = 1.2 \frac{\kappa A}{a} \sqrt{\frac{T}{\pi}}.\]

Substituting for \(a\) in terms of the conductivity \(\kappa\), the capacity for heat of unit volume of glass \(s\), this becomes \(1.2 \Lambda \sqrt{(\kappa s T/\pi)}\).

Putting in the numerical values corresponding to our experiments \(\kappa = 0.0021\), \(T = 540\), \(s = 0.5\), \(\Lambda = 0.21\), the correction is found to be \(0.12\).

3. Correction for Leads.—On the other hand, the water-equivalent of the coil was slightly over-estimated as the wires serving as leads were reckoned in, although part of them protruded out of the water. The length which was outside the water was 2.8 centims., but about 8 millims. of this was in close contact with stout copper rods, the temperature of which would not rise appreciably during the experiment. From the previous investigation, which is applicable to this case, it would appear that one-third or 0.7 centim. of the part surrounded by non-conductors should have been taken into the water-equivalent instead of the whole. The error committed in the heat capacity of 2.1 centims. of copper wire, weighing 0.22 grams. per centim., that is 0.08,
should be subtracted from our water-equivalents, as there were two such wires. The heat produced by the current in the leads (No. 14, I.W.G.) would, if entirely used to raise the temperature of the leads, produce a rise of 0°2 in the time of the experiment. If the whole of this heat is imagined to enter the calorimeter it would produce a difference of 1 part in 150,000 in the total rise. No error can therefore arise through the heating of the leads.

4. Correction for the parts of the Calorimeter not in contact with Water.—The water in our calorimeter reached to about 1°5 centims. from the top of the vessel, but a rough estimate of the error introduced will show that we were justified in taking the whole of the calorimeter into the water-equivalent. The cooling which took place when the temperature of the calorimeter was at 1° above that of the surroundings amounted to 3°5 gramme-degree units per minute. If we assume that the heat lost was the same at every part of the calorimeter, we find that the loss due to radiation and convection of the part of the outside surface above the level of the water amounted nearly to one quarter-unit. The loss of heat towards the inside of the part not filled with water must have been small, but in order to over-estimate the loss we may assume that the part of the calorimeter which was above the water lost 0°3 heat unit per minute for a difference in temperature of 1°. This will allow us to calculate the temperature gradient along the copper close to the water surface. If $\kappa$ is the conductivity of the copper, $A$ the area of the section of the calorimeter, $t$ the time,

$$\kappa tA \frac{du}{dx} = \cdot 5,$$

and since $\kappa$ is nearly unity and $A = \cdot 33$, $\frac{du}{dx}$ is found to be nearly $\cdot 01$. The calculated temperature gradient of $\frac{100}{1°}$ of a degree per centim. must have exceeded considerably the actual one, and must diminish with the distance from the water surface, but assuming it to be uniform all over the upper part of the calorimeter, the average temperature of the copper would be $0°\ 007$ below the temperature of the water. The heat capacity of that part of the calorimeter is approximately unity, and therefore the error in the water-equivalent, considerably over-estimated, is $\cdot 007$, a negligible quantity.

5. Correction for Cork Supports.—It only remains to discuss whether the cork supports on which the calorimeter stood added in any appreciable way to the water-equivalents. It is not possible here to estimate the effect by calculation, as the contact between the calorimeter and the cork is irregularly distributed over the cork.

We therefore made a few experiments in which the change in temperature of the cork was directly measured by means of thermo-junctions, the calorimeter being treated exactly as during an experiment on the heat-equivalent. We found in this way that the heat which entered the three corks during the whole duration of the experiment is only $\cdot 08$ unit as against 3300 units which have entered the water in the calorimeter, and as the greater part of this heat is allowed for in the cooling correction, no addition need be made to the water-equivalents on this account.

MDCCCXCV.—A.
The sum of the various small corrections to the water-equivalent amounts to 0.33, or about 2 parts in 10,000 of the whole water-equivalent.

*The Auxiliary Current.*

In the first two series of our experiments, the thermometer was generally rising during the first, but falling during the last period. It is known that a falling thermometer will somewhat lag behind the real temperature, but we had hoped to eliminate this by applying a constant correction. Special experiments made for the purpose did not, however, give us sufficiently consistent results, and it appeared that the lag was too variable to be allowed for. Hence we decided to work only with a rising thermometer. We might have achieved this by raising sufficiently the temperature of the surrounding water-jacket, but this would have made the gain by radiation and conduction in the first period greater than we thought could be correctly measured. The plan we adopted consisted in sending through our coil, in the final period, a weak current (about 0.1 ampère) which just overbalanced the cooling. The current—which we call the auxiliary current—could be measured with sufficient accuracy to calculate the rate of heating which was due to it alone, and as the rise in temperature was observed, the loss by radiation could be deduced.

The auxiliary current was derived from two storage cells and was measured by one of Lord Kelvin's magnetostatic centiamperemeter balances placed in circuit with the coil and cells. In order to avoid any error that might arise from a possible change in the constant of the instrument due to a change in the value of the earth's
magnetism, we took the precaution of calibrating the instrument immediately after each equivalent experiment. This was done as follows:—

The current from two storage cells passed in succession through the current meter, a coil of manganin wire and a set of adjustable resistances (see fig. 6). The terminals of the manganin coil were connected up through the astatic galvanometer with our Standard Clark cell, so as to oppose the E.M.F. at the terminals of the manganin coil due to the passage of the current from the storage cells to the E.M.F. of the Clark cell. If the galvanometer shows no deflection on both circuits being closed, then \( e = iv \), where \( e \) = E.M.F. of the Clark, \( i \) = current in the current meter, \( v \) = the resistance of the manganin coil.

A coil of manganin wire was chosen, since this material has a very small temperature coefficient; it was supplied by Messrs. Elliott, having a composition of copper 84 per cent., manganese 12 per cent., nickel 4 per cent.; its resistance value was nearly 14 true ohms. An example will explain the calculation of the value of the current. On May 20 the current meter read 48·34 divisions (a short focus lens enabled us to read the divisions to hundredths). Temperature of the Clark cell 17°12 C. Hence the current is equal to \( 14327/14 = 0·10234 \) ampère; and therefore 1 division = 0·00212 ampère. The instrument remained very constant throughout the equivalent experiments, as may be seen from the following table:—

<table>
<thead>
<tr>
<th>Date</th>
<th>Value in amperes of 1 division.</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 10</td>
<td>0·00213</td>
</tr>
<tr>
<td>&quot; 13</td>
<td>0·00212</td>
</tr>
<tr>
<td>&quot; 17</td>
<td>0·00212</td>
</tr>
<tr>
<td>&quot; 20</td>
<td>0·00212</td>
</tr>
<tr>
<td>June 5</td>
<td>0·00212</td>
</tr>
<tr>
<td>&quot; 9</td>
<td>0·00212</td>
</tr>
<tr>
<td>&quot; 15</td>
<td>0·00212</td>
</tr>
</tbody>
</table>

As a check upon this method of calibrating the current meter, it was also calibrated on one occasion by measuring the current passing through it by the silver voltameter. Its constant as thus determined was 0·00212. The sensibility of the current meter was such that its readings were accurate to 1 in 400. Hence the cooling correction to be applied is accurate to 1 in 200, and from the data already given it appears that an error of that amount only affects the accuracy of the equivalent to 1 in 200,000. Knowing the value of the auxiliary current, the rise in temperature \( \theta \) per minute of the total mass of water is calculated from the formula \( \theta = (C^\theta R \times 60) / (J \times M) \), \( R \) being the resistance of the heating coil. The mean of several determinations of \( R \) with an Elliott P.O. box—which had been
sent to Messrs. Elliott for careful examination—gave a value of 31'32 B.A. units at the mean temperature of the equivalent experiments, or 30'90 true ohms, if 1 B.A. unit = .9866 true ohm. It is clear that an approximate value of J will be sufficient in this part of the calculations. Any error in the value of J will affect the cooling correction to half its value, and as that correction amounts to 1 per cent. of the equivalent, an error of 1 per cent. in the assumed value of J would involve an error of 1 part in 20,000 of the final value. The reductions had naturally to be made before we knew what our own value of J was going to be, so we applied provisionally Mr. Griffiths' value of 4'194 X 107, and although our own value is slightly lower it would have made no appreciable difference if our value had been taken instead.

The Temporary Coil.

The only part of the arrangement which has not so far been described is a coil of platinoid equal in resistance to the one in the calorimeter, in series with a resistance approximately equal to that of the silver voltameter.

This coil and resistance served for a preliminary adjustment of the circuit. It was necessary, in order to secure sufficient accuracy, that a balance of electromotive force should be obtained soon after the beginning of each experiment, and this could be done by means of this coil, which, for distinction, we shall call the temporary coil. The keys which serve to change currents were all made of paraffin blocks, and of very simple construction. The blocks had six holes filled with mercury, and copper connectors completed the circuit. The two ways in which connection could be made may be seen in the key marked k2 (fig. 5), where the holes are numbered. In the position of the key which we shall call a, the cups 1 and 3 were connected, as well as 2 and 4; while, in the position b, 1 was connected to 5 and 2 to 6. The keys k3 and k4 were exactly similar, and we shall speak of the positions a and b of the keys when the corresponding connections were made. Thus, k3 (a), k4 (b) means that the key k3 was in position a, and key k4 in position b. The key k4 served to short-circuit the silver voltameter in the final period; a copper connector could be placed for this purpose either at a or b.

Method of Maintaining a Constant Difference of Potential at the Terminals of the Heating Coil.

The difference of potential at the terminals of the heating coil was kept constant by balancing it against the battery of twenty Clark cells in the well-known way. The success of this method, when the potential difference had to be kept constant for some minutes, depends on the ability of the operator in altering the total resistance of the circuit through which the current is passing by small variable amounts. The current—which, in our experiments on the heat-equivalent, was about 0.9 ampere—tends to
diminish in value, owing to (1) change in the values of the different resistances in circuit, due to change of temperature produced by the passage of the current; (2) change of the resistance of the silver voltameter; (3) running down of the electromotive force of the storage cells. In order to counteract the effects of these changes, a number of separate resistances, $W_1$, $W_2$, $W_3$, and two switches $s_1$ and $s_2$ (fig. 5), were placed in series with the remainder of the circuit. $W_1$ consisted of coils of platinoid wire; $W_2$ and $W_3$ were platinoid wires of different resistance-values, any number of which could be connected in series by means of mercury cups and copper bridges. The resistances $W_1$, $W_2$, $W_3$ enabled the current to be adjusted to the proper value when running through the temporary circuit; $W_3$ or $W_3$ enabled us to make any necessary change at the moment of sending the current through the heating coil. The switches $s_1$ and $s_2$ were used to keep the spot of light in the zero position during the nine or ten minutes the current was passing through the heating coil. They consisted of a stone base, on which were arranged eleven brass studs (shown in figure) along a semicircle, having binding screws (not shown) attached to their ends. Over these studs slides a movable contact piece attached to an insulating handle. The movable arm consists of a number of thin brass plates, jointed together only at the centre, and so fitting that they form independent springs which press edgewise on the brass studs, thus ensuring good uniform contact. The resistances to be inserted are placed in the binding screws attached to the studs (soldered to ensure better contact). One switch had platinoid wires of 0.008 ohm, and the other platinoid wires of 0.006 ohm. These switches gave a much greater range than was found necessary in any experiment. When the spot of light was observed to move from the zero position, a movement of the arms of these switches brought it back. The spot of light was never as much as five small divisions from its position of rest, but even a deviation of ten divisions during the whole time of the experiment would have produced no appreciable difference in the value of the equivalent.

The current was only switched on to the principal circuit when it was found to be running with fair steadiness through the temporary circuit. After some little trouble, caused by leakage, we were able to keep the current constant without any considerable change in the value of the total resistance of the circuit.

The electromotive force that is thus measured is the difference of potential at the terminals of the heated coil, provided there is no leakage in the wires connecting these terminals to the galvanometer. The insulation of these wires was found to be $7 \times 10^8$ ohms, so that the electromotive force at the galvanometer is practically equal to the electromotive force at the terminals of the coil.

Method of carrying out an Experiment.

Two observers were required to carry out an experiment; one (A) kept the electromotive force at the ends of the coil constant and compared the Clark cells; the other (B) took all the temperature observations,
A weighed and measured quantity of water having been placed in the calorimeter, the platinum dish (after being weighed several times) was filled with 120 cub. centims. of the silver nitrate solution. The water in the jacket of the calorimeter was raised about 1° C. above the temperature of the water in the calorimeter, so as to secure a convenient rise before the heating of the coil commenced. The observations are conveniently divided into three periods. The reference to the connections will be understood with the help of fig. 5.

Preliminary Period.

A, being the main battery, the key Q was open at first, and the connections in the other keys were as follows: k₂ (a), k₃ (a), k₄ (a). The observer (A) compared the Clark cells with the help of the key k₁, and at the conclusion of the comparisons—which took about 8 minutes—the temporary bridges of k₁ were removed. (A) then closed the main circuit at Q, and the connections were such that the current was flowing through the temporary coil and could be adjusted till a balance was obtained against the 20 Clarks C.B. The observer (B) in the meantime observed every minute the thermometer which was plunged into the calorimeter. The rise was roughly about 0°-002 per minute, and so regular that more frequent observations would have been of no value. (B) also observed the auxiliary thermometers.

Everything being ready, a signal was given 10 seconds before the current was to be sent through the principal coil. (B) now broke connections at k₂ and joined k₃ (a).

Main Period.

(B) changed the connection k₄ (a) to k₄ (b), and the main current thus passed through the coil in the calorimeter. A signal being given that this was done, (A) makes connections k₂ (b), and thereby opposed the Clark battery to the electromotive force at the terminals of the principal coil. If the preliminary adjustment was perfect (as it was on two occasions), the spot of light remained at rest; but generally it moved slightly to one side, and then a slight readjustment of the resistances brought it back to its position of rest. (A) called out when he had obtained a satisfactory balance, and this was generally three seconds after the main current was complete. As the experiment lasted nine or ten minutes, and as the electromotive force was never as much as two in a thousand out during the first three seconds, no error in the final result can be introduced in this short period. During the heating of the coil (B) did not take any temperature observations except when half the proposed time of heating had elapsed. The object of this observation is to be able to point the telescope very near the division of the thermometer which the mercury thread would reach at the conclusion of the experiment.

Final Period.

Ten seconds before the main current was interrupted, the connection at k₃ was broken, the balance being always so steady that it could be trusted to be maintained during that interval. (B) now broke k₃ (a), and three seconds after connected k₃ (b).
(A) in the meantime had changed $k_2$ from $a$ to $b$, $k_1$ being still at $b$. The circuit is now seen to be such that the small battery $A_2$ sends a current through the magnetostatic meter $M$ and the calorimeter coil. In this final period (B) observed the thermometer and the magnetostatic meter, and also made observations on the auxiliary thermometers placed near the stem of the Baudin, in order to introduce the stem correction. (A) once more compared the Clarks.

**The Results.**

We divide our experiments into three series, but only attach any value to the third, as during the first two sets the thermometer was falling in the last period. We had hoped, at first, to be able to apply a small correction, to eliminate the error which is due to the fact that a falling thermometer will read too high, and we made a large number of experiments to determine the correction. We arrived, however, at the result that the indications of a falling thermometer are so irregular that no correction is possible. Consequently in our third series the thermometer was rising during the whole course of each experiment.

We think it worth while to put on record an impression that the behaviour of our Baudin thermometer has altered since we received it from the maker. As soon as it came some preliminary experiments were made, to see if we could work with the thermometer while it was falling, and the observations seemed to show that the fall was sufficiently uniform. Our first three experiments gave results which were very consistent, and a minute after the current was broken the temperature seemed to fall already in a perfectly regular manner. But as we continued our work, the behaviour of the instrument seemed to deteriorate. Thus in our experiment of March 8th the thermometer had hardly fallen three minutes after the current had stopped. It is possible that this was due to accidental circumstances, for it is well known that different places in the bore of a capillary tube behave very differently. We wish therefore to express no opinion at present as to the probability of an actual change in the behaviour of the thermometer, but only to draw the attention of other experimenters to this point which seems worth keeping in mind.

The results of the first three experiments which constitute the first series are consistent, but no value is attached to the equivalent as deduced from them, owing to the uncertainty of the water equivalent. The coil, as has been mentioned, was then wound on an ivory frame. When Mr. Hadley, who then assisted in the work, began to experiment on the specific heat of ivory, he met with serious difficulties. The ivory contained water to begin with, as was shown by the diminution in the weight of fresh ivory when heated up; it absorbed again when placed in water; the results were consequently not to be trusted. Even when coated with shellac, the substance did not behave in a consistent manner. There were other imperfections in our calorimeter at that time which make it impossible for us to know the water equivalent with sufficient accuracy.
In the second series of experiments, the coil was wound on porcelain strips, and we were quite satisfied that the water equivalent was known with sufficient accuracy. Nevertheless the agreement of the results in this series is not satisfactory.

In experiments 4 and 6 the thermometer was falling both in the first and last period, and the cooling correction was consequently somewhat large; on the other hand the lag of the falling thermometer would affect both the first and last period, and, therefore, be partly eliminated in the result.

Experiment 5 is rendered a little uncertain by the fact that the thermometer at the beginning of the first period fell slightly, and then remained perfectly stationary; it is therefore probable that the temperature was really increasing at the beginning of the experiment. The cooling correction, calculated on the assumption of no rise, would be too large, hence the calculated equivalent too small. The result of March 8th is anomalous, and does not seem altogether accounted for by the sticking of the thermometer at the end. There was on that day an exceptionally large difference in the amount of water, as measured by weight and by volume. We took, as usual, the mass as determined by weight; had we taken the latter, the calculated equivalent would have been 4181. A final revision of our calibration correction showed a small error, which may have affected some of the results in series I. and II., by about one part in two thousand. As we do not attach any value to the numbers obtained, we have not recalculated the numbers.

The results of our third series are as consistent as could be hoped for. We thought it useless to multiply the experiments, as it did not seem to us that our results could be materially improved by repetition. Their good agreement shows that our results are correct to more than one part in a thousand, provided that we have avoided systematic errors. The difference between our results and that of Mr. Griffiths must be due, on the one side or other, to errors which a multiplication of experiments could not eliminate.

We give the results of our experiments in the form of Tables.

Column I. gives the number of the experiment.

Column II. gives the date.

Columns III. and IV. state whether in the first and last period respectively the thermometer was falling or rising.

Column V. gives the value of the equivalent calculated, the temperature scale being that of a mercury thermometer made of French hard glass.

Columns VI. and VII. give the same equivalent, reduced to the nitrogen and hydrogen scale of the Bureau International des Poids et Mesures.

Column VIII. gives the temperature range of the experiment.
DETERMINATION OF THE SPECIFIC HEAT OF WATER.

Table X.

Series I.

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
</tr>
</thead>
<tbody>
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<td>Rising</td>
<td>Falling</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>15.2–17.2</td>
</tr>
<tr>
<td>2</td>
<td>&quot; 5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>16.6–18.8</td>
</tr>
<tr>
<td>3</td>
<td>June 9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>19.9–21.9</td>
</tr>
</tbody>
</table>

Mean... $4\times 10^7$ $4\times 10^7$ $4\times 10^7$ 17.3–19.3

Table XI.

Series II.

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
</tr>
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<tr>
<td>4</td>
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<td>Falling</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>15.2–17.2</td>
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<tr>
<td>5</td>
<td>&quot; 12</td>
<td>&quot;</td>
<td>&quot;</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
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<td>6</td>
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<td>Falling</td>
<td>&quot;</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>16.4–18.6</td>
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<tr>
<td>7</td>
<td>&quot; 22</td>
<td>Rising</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>16.4–18.6</td>
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<tr>
<td>8</td>
<td>Mar. 1</td>
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<td>&quot;</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>16.4–18.6</td>
</tr>
<tr>
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<td>&quot; 8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>16.4–18.6</td>
</tr>
</tbody>
</table>

Mean... $4\times 10^7$ $4\times 10^7$ $4\times 10^7$ 15.9–18.1

Table XII.

Series III.

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
<th>V.</th>
<th>VI.</th>
<th>VII.</th>
<th>VIII.</th>
</tr>
</thead>
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<td>10</td>
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<td>Rising</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>17.4–19.6</td>
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<td>&quot;</td>
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<td>$4\times 10^7$</td>
<td>17.2–19.4</td>
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<tr>
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<td>&quot; 20</td>
<td>&quot;</td>
<td>&quot;</td>
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<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>17.3–19.7</td>
</tr>
<tr>
<td>13</td>
<td>June 5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>17.2–19.4</td>
</tr>
<tr>
<td>14</td>
<td>&quot; 9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>15.2–19.2</td>
</tr>
<tr>
<td>15</td>
<td>&quot; 15</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>$4\times 10^7$</td>
<td>16.2–19.4</td>
</tr>
</tbody>
</table>

Mean of first four... $4\times 10^7$ $4\times 10^7$ $4\times 10^7$ 17.4–19.7

" last two... $4\times 10^7$ $4\times 10^7$ $4\times 10^7$ 19.2–21.4

" Series III... $4\times 10^7$ $4\times 10^7$ $4\times 10^7$ 18.0–20.3

MDCCXCV.—A. 3 N
Our final value is

\[ J = 10^7 \times \begin{cases} 
4.1804 \text{ on the mercury scale of hard French glass}, \\
4.1905 \text{ on the nitrogen scale}, \\
4.1917 \text{ on the hydrogen scale}, 
\end{cases} \]

at a temperature of 19°.1.

This result depends on the assumption that the electrochemical equivalent of silver is 0.001118, and that our standard Clark cell had an electromotive force of

\[ 1.4340 \left(1 - \alpha t - 15\right) \text{ volts}, \]

where \( \alpha = 0.00814 + 0.00007 (t - 15) \) as given by Kahle ('Zeitschrift für Instrumentenkunde,' vol. 13, p. 310, 1893). Glazebrook and Skinner's coefficient refers to a mean temperature of 7°.5, and is identical with the above at that temperature.

**Discussion of Results.**

The comparison of the results of different observers will be facilitated by Table XIII., in which we compare ergs with the foot-pound at Greenwich and the kilogram-metre at Paris.

<table>
<thead>
<tr>
<th>Table XIII.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ergs \times 10^{-7}.</strong></td>
</tr>
<tr>
<td>4.160</td>
</tr>
<tr>
<td>4.165</td>
</tr>
<tr>
<td>4.170</td>
</tr>
<tr>
<td>4.175</td>
</tr>
<tr>
<td>4.180</td>
</tr>
<tr>
<td>4.185</td>
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<tr>
<td>4.190</td>
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<tr>
<td>4.195</td>
</tr>
<tr>
<td>4.200</td>
</tr>
<tr>
<td>4.205</td>
</tr>
<tr>
<td>4.210</td>
</tr>
</tbody>
</table>

This table has been calculated on the assumption that \( g \) at Paris is equal to 980.96, and at Greenwich equal to 981.24.

We have prepared another table (XIV.) which will give at any temperature the correction of an interval measured on our mercury thermometer to an interval measured on the nitrogen and hydrogen thermometers. This table has been calculated with the help of the equation given by Chappuis for the correction to the thermometer made of French hard glass.
In comparing our results with those of other observers, we have in the first place to consider the value which Mr. Griffiths has obtained in his very excellent series of measurements. His final result ('Proc. Roy. Soc.,' vol. 55, p. 26; Phil. Trans., vol. 184, 1893, A., p. 361), is

\[ J = 4.1982 \left(1 - 0.00266 \frac{\theta}{15}\right) \times 10^7. \]

This refers to the nitrogen thermometer. At a temperature of 19°, the value would be reduced to 4.1936, which corresponds to our 4.1905 at the same temperature. Griffiths' value is to be increased slightly owing to the fact that he really measures the difference between the specific heat of water and of air. This would increase the value of \( J \) by 0.011 about, so that the value of \( J \) at 19° would be raised to 4.1947 \( \times 10^7 \), which is exactly one part in a thousand larger than ours. The difference is small, but must be due to some systematic error, as both Griffiths' value and our own agree so well with each other, that ordinary observational errors and accidental disturbance could not have produced so large a difference in our result. The least satisfactory part of a calorimetric measurement must always be the cooling correction, and we have considered it of great importance to reduce that correction as much as possible. The uncertainty of the cooling correction does not necessarily depend on its value; thus, we can much diminish it by starting, as we have done in our last series, with the initial temperature of the calorimeter about as much below that of the water-jacket as the final temperature is above it. Yet the uncertainty of the correction does not seem to us to be diminished by that process. We may reasonably estimate the uncertainty due to the cooling correction by calculating what the error in the observed rate of cooling, either at the beginning or end of the experiment, must have been in order to produce a difference of one part in a thousand in the final result. We find in our own experiments that the error must have amounted to more than 15 per cent. We consider it unlikely that so large an error occurred always in the same direction. Apart from the cooling correction, however, it is difficult to see how a difference of one-tenth per cent. is produced unless by accumulation of a number of small errors.
The weak point of Mr. Griffiths' determination is the small quantity of water he uses, his result depending on the introduction of about 120 grams into his calorimeter. The highest water equivalent with which he worked was about 250 grams, of which 85 are due to the calorimeter itself. The chief objection to the use of such small quantities lies in the great cooling correction. In the experiment quoted by him on p. 482, the loss of heat due to radiation and conduction at the end of his experiment amounts to about 9 per cent. of his heat supply. If such loss has been wrongly estimated to 1 per cent., an error of \( \frac{1}{10} \) per cent. would result in the final value. The consistency of Mr. Griffiths' results shows that if an error occurred due to that cause, it must have been systematic, and we may point out how, with such large cooling correction, serious errors may arise. In applying the cooling correction it is always assumed that the loss of heat depends only on the difference of temperature between the calorimeter and enclosure; but, as has been already pointed out, this is not the case as regards conduction. Mr. Griffiths' calorimeter was suspended by three stout glass tubes, through one of which the stirrer was passing. The exhaustion in the space surrounding the calorimeter was never sufficient to do away with the conduction of air, so that we may take the larger part of the cooling to be due to conduction and convection. The loss of heat in that case must to some extent depend not only on the temperature, but on the rate of change of temperature. Whether the part which depends on the rate of change is sufficient to produce a sensible difference in the result, it is not easy to say, but the error produced would with different currents and quantities of water be the same in all cases, and could not, therefore, be detected by the inconsistencies thereby introduced into the results.

The difference between our value of the equivalent and that of Mr. Griffiths is, however, of smaller importance than the difference which exists between them and the equivalent, as determined directly by Joule, Rowland, and Miculescu. Joule's latest value, which is the only one which needs consideration, is 772.65 foot-pounds at 61°.7 Fahrenheit. The number refers to the degree as measured by Joule's mercury thermometer. Rowland adds to this a correction to the air thermometer of about 3, and another small correction for a change in the heat capacity of the apparatus, which brings the value up to about 776. The correction to the air thermometer has been obtained by means of a comparison made by Joule himself with one of Rowland's thermometers. Joule's original thermometers have been temporarily placed by Mr. B. A. Joule in the hands of Professor Schuster, in order that an accurate comparison may be instituted between them and modern thermometers. A full description of the comparisons made will be given on another occasion. The result arrived at shows that the correction is less than that assumed by Rowland, and would bring his value up to only 775 at the temperature indicated.

Griffiths compares his result with that deduced by Rowland from Joule's observations. Rowland combined the different values obtained by Joule in his various investigations, attaching weights according to his judgment as to their relative
merits. Griffiths finds in this way that the difference between himself and Joule amounts to one part in 350, but, if equal weights are attached to all Joule's results, the difference is reduced to one part in 4281. Little value can be attached, however, to a combination of Joule's results which gives equal weights to that obtained in 1847 and that deduced from his latest and most careful work. There is, moreover, in Rowland's table a misprint or error in the reduction of Joule's 1847 result from foot-pounds to kilogram-metres, which lowers the value as given by Griffiths from 779-2 to about 778. It does not seem to us advisable to go beyond Joule's 1878 results, and the value assigned by him in this latest research should be taken as giving his final judgment on the matter. Reducing to the nitrogen thermometer of the Bureau International, Joule's result is 775 foot-pounds at Greenwich, at a temperature of 16°-5 C. At the same temperature Griffiths' number is 779-8.

Great weight must be attached to Rowland's determination, which, at the temperature to which Joule's number applies, is 777-6, and at 19°-1, 776-1, corresponding to our 778-5. Rowland's value is, therefore, just halfway between our own and Joule's result. But it must be taken into consideration that if the comparison between Rowland's and Joule's thermometers, as made by the latter, is to be trusted, Rowland's value referred to the "Paris" nitrogen thermometer would be slightly reduced. At any rate, it seems probable that if his value is in error, it is rather in the direction of being too high. We have, therefore, a difference of at least three parts in a thousand to account for between our result and that of Rowland, and of nearly four parts in a thousand between Griffiths' and Rowland's at a temperature of 19°-1. These results are summarised into the following table:—

Table XV.—Equivalent in foot-pounds at Greenwich, at 19°-1, referred to "Paris" nitrogen thermometer.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>774</td>
<td>776-1</td>
<td>779-1</td>
<td>778-5</td>
</tr>
</tbody>
</table>

We now turn to an investigation by Miculescu ('Annales de Chimie et de Physique,' vol. 27, 1892) in which the mechanical equivalent of heat is measured directly by what seems an excellently devised series of experiments. His result is 4-1857 x 10⁷. He does not state the exact temperature to which this applies, but all his experiments seem to have been made between 10° and 13°, so that we may assume 11°-5 to be the mean temperature of his experiments. Rowland's value at that temperature is 4-199 x 10⁷. We must draw attention to one point in Miculescu's work, which requires clearing up before we can give to it any decisive
value. Everything in the experiments depended on the measurement of a couple, the arm of the couple being the distance between two knife-edges, one of which had to support a weight of more than 43 kilos. The distance between the knife-edges is said to have been 28 centims. in all experiments. Very insufficient information is however given how that distance was measured, and it would almost seem as if the author had trusted to the maker in adjusting the central knife-edge to the zero point of its scale. If the apparatus is still in existence it might be well to make sure that no error has been introduced through a wrong estimate of the length of the lever arm.

In order to compare Miculescu's value with that of others we must apply a temperature correction which is somewhat doubtful, but taking the mean of Rowland's and Griffiths' values as the most probable at present, we obtain at 15° the following values:

Table XVI.—Equivalents in foot-pounds at Greenwich, at 15°, referred to the "Paris" nitrogen thermometer.

<table>
<thead>
<tr>
<th>Joule</th>
<th>Rowland</th>
<th>Miculescu</th>
<th>Griffiths</th>
<th>Schuster and Gannon</th>
</tr>
</thead>
<tbody>
<tr>
<td>775</td>
<td>778.3</td>
<td>776.6</td>
<td>780.2</td>
<td>779.7</td>
</tr>
</tbody>
</table>

If we remember that Rowland's number referred to the "Paris" nitrogen thermometer would probably be smaller by one unit, we are struck with the fair agreement there is on one hand between the results of Joule, Rowland, and Miculescu, and, on the other hand, between Griffiths and ourselves. As far as we can draw any conclusions from the comparison, it seems to point to a difference in the value obtained by the electrical and direct methods. Whether this method is due to some remaining error in the electrical units or to some undiscovered flaw in the method adopted by Mr. Griffiths and ourselves remains to be decided by further investigations.
Appendix.

We give the observations and the calculation of the result of the experiment on 20th May, which is typical of the other experiments. The symbols used are the same as those on pp. 421 and 422.

(1.) The Electromotive Force.—Comparison of the Clark cells.

<table>
<thead>
<tr>
<th>Before the experiment</th>
<th>After the experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Time:</strong> 11h 43m</td>
<td><strong>Time:</strong> 12h 16m</td>
</tr>
<tr>
<td>$t_1' = 17^\circ 06'$</td>
<td>$t_5' = 17^\circ 23'$</td>
</tr>
<tr>
<td>I.— Standard = $-3'2$ ($a_1$)</td>
<td>I.— Standard = $-4'0$ ($a_6$)</td>
</tr>
<tr>
<td>II.— '' = $-4'6$</td>
<td>II.— '' = $-5'8$</td>
</tr>
<tr>
<td>III.— '' = $+1'0$</td>
<td>III.— '' = $+0'5$</td>
</tr>
<tr>
<td>IV.— '' = $+1'4$</td>
<td>IV.— '' = $+0'5$</td>
</tr>
<tr>
<td>V.— '' = $-0'5$</td>
<td>V.— '' = $-1'0$</td>
</tr>
<tr>
<td>VI.— '' = $-0'7$</td>
<td>VI.— '' = $-1'8$</td>
</tr>
<tr>
<td>VII.— '' = $+1'4$</td>
<td>VII.— '' = $+0'3$</td>
</tr>
<tr>
<td>VIII.— '' = $-0'1$</td>
<td>VIII.— '' = $-1'4$</td>
</tr>
<tr>
<td>IX.— '' = $ +2'4$</td>
<td>IX.— '' = $+1'4$</td>
</tr>
<tr>
<td>X.— '' = $ +2'0$</td>
<td>X.— '' = $+1'2$</td>
</tr>
<tr>
<td>$s_1 = -0'9$</td>
<td></td>
</tr>
<tr>
<td>I.— Standard = $-4'0$ ($a_5$)</td>
<td>I.— Standard = $-4'0$ ($a_5$)</td>
</tr>
<tr>
<td>$t_5' = 17^\circ 12$</td>
<td>$t_5' = ?$</td>
</tr>
<tr>
<td>Set 1.—(I. + II. + ... + X.) = $+4'0$</td>
<td>Set 1.—(I. - II. + ... + X.) = $+15'0$</td>
</tr>
<tr>
<td>Set 2.—(I. + II. + ... + X.) = $+2'0$</td>
<td>Set 2.—(I. - II. + ... + X.) = $+13'2$</td>
</tr>
<tr>
<td>I.— Standard = $-3'2$ ($a_5$)</td>
<td>I.— Standard = $-4'1$ ($a_5$)</td>
</tr>
<tr>
<td>$t_5' = 17^\circ 17$</td>
<td>$t_5' = 17^\circ 17$</td>
</tr>
<tr>
<td><strong>Time:</strong> 11h 53m</td>
<td><strong>Time:</strong> 11h 06m</td>
</tr>
</tbody>
</table>

The observations in the column headed "After the experiment" were made from below upwards, the interval between 11h 53m and 12h 06m being taken up by the experiment on the equivalent. The correction due to temperature change here is

$$5 \times (a_3 - a_1 + a_4 - a_6) = 0'5.$$

Hence

Set (1) + Set (2) = 20 standards + 6'6 (see p. 422).

As the total resistance of the circuit differed very little from 10,000 ohms, and the electromotive force of the Leclanché used was 1'45 volts, the correction to the battery of Clark's becomes $6'6 \times 1'45 \times 10^{-4} = 0'0010$ volt.
The average temperature of the Clark cells during the above experiment was 17°5. Hence the electromotive force calculates out as follows:—

20 Clark cells at 15° C. . . . . . . 28.6800 volts.
Correction to 17°15, taking the change for each cell to be 0.00115 volt per degree \( \frac{-0.0493}{0.00115} \),
Correction of battery to standard . . . + 0.0010 ,,

Electromotive force of battery . . 28.6317 ,, (E).

\[ \text{(2.) Total Water Equivalent.} \]

Calorimeter + coil . . . . . . . . . . . 270.14 grams.
Calorimeter + coil + water . . . . . . . 1781.54 ,, (At 12° 45\text{"}.)

Hence

Water . . . . . . . . . = 1511.40
Evaporation correction . . = 0.05
Buoyancy ,, . . = 1.58
Equivalents \( \begin{align*} 27.02 \\ 0.34 \end{align*} \) . . . = 27.36

Total water . . . 1540.39 (W).

The equivalents include 27.02, the constant value throughout all the experiments (see p. 441), and 0.34 for the part of the thermometer stem above 12°, which was immersed in the water.

\[ \text{(3.) Weight of Silver Deposit.} \]

<table>
<thead>
<tr>
<th>Date of Weighing</th>
<th>Observed weight of dist.</th>
<th>Temperature</th>
<th>Barometer</th>
<th>Temperature correction in milligrams</th>
<th>Barometer correction in milligrams</th>
<th>Corrected weight</th>
<th>Mean</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 19</td>
<td>64.263487</td>
<td>17.0</td>
<td>749.7</td>
<td>+ 0.940</td>
<td>+ 0.076</td>
<td>64.263603</td>
<td>-62034</td>
<td></td>
</tr>
<tr>
<td>&quot; 20</td>
<td>26.3510</td>
<td>16.9</td>
<td>740.9</td>
<td>+ 0.938</td>
<td>+ 0.074</td>
<td>26.3622</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; 23</td>
<td>88.3859</td>
<td>16.9</td>
<td>758.2</td>
<td>+ 0.938</td>
<td>+ 0.013</td>
<td>88.3910</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; 23</td>
<td>88.3943</td>
<td>17.0</td>
<td>758.2</td>
<td>+ 0.940</td>
<td>+ 0.013</td>
<td>88.3966</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The silver deposit was thus 0.62034 gram. (W).
The weighings are supposed to be correct to .1 millim., and in the mean of any two observations the second decimal may be retained as having some significance. The temperature and pressure corrections were calculated for safety to .001 millim., and it was found more convenient to carry out the calculations to that place, cutting off the unnecessary figure at the end.

(4.) **Temperature Observations.**

The temperature was measured by subdividing a thermometer division of 0°-02 to the 100th part by the eye; each reading is probably right to 0°-0004.

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>h. m.</td>
<td>°</td>
<td>h. m.</td>
<td>°</td>
</tr>
<tr>
<td>11 48</td>
<td>17.2200</td>
<td>12 11</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>90</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2312</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2432</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2516</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2604</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>36</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>12 00</td>
<td>86</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Circuit made</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

By the method of least squares, we obtain from the preceding observations:

- **Mean rate of rise per minute in the first period** = 0°-00406
- **Temperature at 12h 1m** = 17°-2722
- **Mean rate of rise per minute in the third period** = 0°-00227
- **Temperature at 12h 12m** = 19°-7508

The readings of the centiampere balance at equal intervals of time were

- 62°06
- 61°86
- 61°46
- 60°56
- 60°36

or a mean reading of 61°26.

MDCCCXCXCV.—A. 30
The calibration of the balance immediately after the experiment showed that 1 division = 0.00212 ampere, so that the mean value of the current flowing through the measuring coil in the final period was equal to 0.12987 ampere. From this and the data: resistance of coil = 31.32 B.A. units, 1 B.A. unit = 1.9866 x 10^9 C.G.S. unit, J. (assumed) = 4.194 x 10^7, total water = 1540.50 grams; we easily obtain that the rise per minute due to auxiliary current = 0°.00484. As the observed rise per minute was 0°.00227, the cooling per minute in the final period was equal to 0°.00257.

We require to know the temperature at 12 h. 11 m. Since the cooling per minute at a mean temperature of 17°.25 was 0°.00406, and at a mean temperature of 19°.76 was +0°.00257, a slight calculation will show that the cooling per minute at 17°.27 was equal to 0°.00401, and at 19°.75 was +0°.00254.

We are now able to calculate the temperature rise.

Temperature at 12 h. 12 m. . . . . . . . = 19°.7508
Rise in temperature during 55 seconds, due to
auxiliary current . . . . . . . . . . . . . . = 0°.0044
Cooling for 1 minute . . . . . . . . . . . . . = 0°.0025
Therefore temperature at 12 h. 11 m. . . . . . . . . = 19°.7489
Calibration correction at this point . . . . . . . = −0°.0054
Therefore corrected temperature at 12 h. 11 m. = 19°.7435
Temperature at 12 h. 1 m. . . . . . . . . . . . = 17°.2722
Calibration correction at this point . . . . . . . = −0°.0050
Therefore corrected temperature at 12 h. 1 m. = 17°.2672
Difference of these temperatures. . . . . . . = 2°.4763

To this difference we must add the following corrections:—

(a) For the cooling during the time the main circuit was closed, 10 x 1/2 (0°.00254 − 0°.00401) = −0°.00735
(b) To correct for the wrong interval of the Baudin thermometer −0°.00135 x 2.47 = −0°.00333
(c) For the emergent stem. . . . . . . . . . . . . = +0°.00126
(a) + (b) + (c). . . . . . . . . . . . . . . . . . . . . . . . . . . . . = −0°.0094
Therefore corrected rise in temperature = 2°.4669(t)

\[ J = \frac{\nu E}{(0.001118 \text{ Wt})} = 4.1807. \]
DETERMINATION OF THE SPECIFIC HEAT OF WATER.

The following Table includes the Values of the Quantities necessary for the Final Calculation of the Heat Equivalent in the Experiments of the Third Series.

<table>
<thead>
<tr>
<th>Date of experiment</th>
<th>Weight of deposit in grams.</th>
<th>Electromotive force</th>
<th>Total water in grams.</th>
<th>Temperature change.</th>
<th>Value of J. on mercury thermometer.</th>
<th>Mean temperature of water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>13th May</td>
<td>0.55938</td>
<td>28.6349</td>
<td>1543.07</td>
<td>2.2200</td>
<td>4.1824 \times 10^7</td>
<td>18.3</td>
</tr>
<tr>
<td>17th</td>
<td>0.55881</td>
<td>28.6330</td>
<td>1540.32</td>
<td>2.2224</td>
<td>4.1807</td>
<td>11.2</td>
</tr>
<tr>
<td>20th</td>
<td>0.62034</td>
<td>28.6317</td>
<td>1540.39</td>
<td>2.4669</td>
<td>4.1807</td>
<td>15.5</td>
</tr>
<tr>
<td>5th June</td>
<td>0.55684</td>
<td>28.6050</td>
<td>1540.41</td>
<td>2.2125</td>
<td>4.1804</td>
<td>19.0</td>
</tr>
<tr>
<td>9th</td>
<td>0.55780</td>
<td>28.5878</td>
<td>1534.34</td>
<td>2.2251</td>
<td>4.1776</td>
<td>19.3</td>
</tr>
<tr>
<td>15th</td>
<td>0.55952</td>
<td>28.5418</td>
<td>1530.91</td>
<td>2.2180</td>
<td>4.1822</td>
<td>21.3</td>
</tr>
</tbody>
</table>
XII. The Oscillations of a Rotating Ellipsoidal Shell containing Fluid.

By S. S. Hough, B.A., St. John's College, Cambridge.

Communicated by Sir Robert S. Ball, F.R.S.

Received January 18,—Read February 7,—Revised March 28, 1895.

Introduction.

In a paper published in 'Acta Mathematica,' vol. 16, M. Folie announces the fact that the latitude of places on the earth's surface is undergoing periodic changes in a period considerably in excess of that which theory has hitherto been supposed to require. This result has been confirmed in a remarkable manner by Dr. S. C. Chandler in America (vide 'Astronomical Journal,' vols. 11, 12), who, as the result of an exhaustive examination of almost all the available records of latitude observations for the last half-century, has assigned 427 days as the true period in which the changes are taking place.

The old theory, based on the assumption that the earth was rigid throughout, led to a period of 305 days, and M. Folie proposes to account for the extension of this period by attributing a certain amount of freedom to the internal portions of the earth. The earth he supposes to be composed of "a solid shell moving more or less freely on a nucleus consisting of fluid at least at its surface." The argument advanced by M. Folie in favour of this constitution of the earth, namely, the independence of the motions of the shell and the nucleus, appeared to me to be unsatisfactory, and I therefore proposed to myself to test the validity of it by examining a particular case which lent itself to mathematical analysis, namely, that in which the internal surface of the shell is ellipsoidal and the nucleus consists entirely of homogeneous fluid.

The principal axes of the shell and of the cavity occupied by fluid are assumed to be coincident, and the oscillations are considered about a state of steady motion in which the axis of rotation coincides with one of these axes. It is clear that a steady motion will be possible in this case, and that such a motion will be secularly stable in the event of the axis of rotation being the axis of greatest moment for both the shell and the cavity.

The problem was originally treated by the analysis used by Poincaré in his memoir on the stability of the fluid ellipsoid with a free surface ('Acta Mathematica,' 25.7.95.)
vol. 7). This analysis reduces the determination of the motion of the fluid to the problem of finding a single function \( \psi \), subject to certain boundary conditions, which in our case take a very simple form. In the case where the surface of the fluid is ellipsoidal, it is found that, when the system is oscillating in one of its normal modes, \( \psi \) will be expressible as the sum of a series of Lamé products of a single order \( n \) only.

When \( n \) is different from 2, the types of oscillation are such that no disturbance of the shell is involved, and a period equation for the oscillations of the fluid may be deduced in a manner similar to that given by Poincaré.

The types of oscillation corresponding to \( n = 2 \) demand exceptional treatment, in consequence of the motion communicated to the shell when they exist. The fluid motion, however, is found to be such that the molecular rotation is everywhere the same. Mr. Bryan has suggested to me that this circumstance may be made use of in order to treat the oscillations which involve motions of the shell by a simple analysis previously employed by Greenhill (‘Proc. Camb. Phil. Soc.’, vol. 4, p. 4) which does not involve Lamé functions. To facilitate the reading of the paper, the results are first deduced by this method, and the Lamé analysis by which they were originally obtained is reserved for an appendix.

The oscillations under consideration are found to be of two types. One of these corresponds to an oscillation previously discussed by Hopkins in his ‘Researches in Physical Geology’ (‘Phil. Trans.’, 1839). This exists only in consequence of the contained fluid, and in it the oscillations of the shell are similar in character to the ‘forced’ nutations of the earth produced by the action of the sun and moon. In the other type the motion of the shell is closely analogous to the motion of a rigid body when slightly disturbed from a motion of pure rotation about a principal axis, and, in fact, identifies itself with such an oscillation in the event of the inertia of the fluid becoming negligible.

On applying the problem to the case of the earth, the latter mode is that on which the variations of latitude depend. The period, however, is found to be shorter than it would be if the fluid were solidified, and thus, in this particular case, M. Folie’s results are contradicted. It appears to me to be highly probable that any such freedom in the interior of the earth as that supposed by M. Folie, provided the surface does not undergo deformation, would have the effect of reducing, instead of extending, the period, and the true explanation of the phenomenon is probably that given by Newcomb (‘Monthly Notices of the Royal Astronomical Society,’ March, 1892), who shows that the elasticity of the earth, as a whole, would have the effect of prolonging the period.

§ 1. The Period Equation.

Let us refer to rectangular axes coincident with the principal axes of the ellipsoidal cavity.
Let \( \alpha, \beta, \gamma \) be the principal semi-axes of this cavity; \( A, B, C \) the principal moments of inertia of the shell.

Suppose the motion of the fluid at any instant consists of a rigid body rotation with angular velocities \( \xi, \eta, \zeta \) about the axes of the ellipsoid, compounded with the irrotational motion consequent on giving the shell additional angular velocities \( \Omega_1, \Omega_2, \Omega_3 \).

The velocity-potential of the irrotational motion will be

\[
\frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} yz \Omega_1 + \frac{\gamma^2 - \alpha^2}{\gamma^2 + \alpha^2} xz \Omega_2 + \frac{\alpha^2 - \beta^2}{\alpha^2 + \beta^2} xy \Omega_3.
\]

The velocity-components will therefore be

\[
\begin{align*}
  u &= \frac{\gamma^2 - \alpha^2}{\gamma^2 + \alpha^2} z \Omega_2 + \frac{\alpha^2 - \beta^2}{\alpha^2 + \beta^2} y \Omega_3 - y \xi + z \eta \\
  v &= \frac{\alpha^2 - \beta^2}{\alpha^2 + \beta^2} x \Omega_3 + \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} z \Omega_1 - z \xi + x \zeta \\
  w &= \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} y \Omega_1 + \frac{\gamma^2 - \alpha^2}{\gamma^2 + \alpha^2} x \Omega_2 - x \eta + y \zeta
\end{align*}
\]

Hence, if \( h_1, h_2, h_3 \) be the components of angular momentum, and \( M \) denote the mass of the fluid, \( \rho_1 \) its density,

\[
\begin{align*}
  h_1 &= \Lambda (\Omega_1 + \xi) + \iint \rho_1 dx dy dz (wy - vz) = \Lambda (\Omega_1 + \xi) + \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} \Omega_1 \\
  &\quad + \frac{1}{6} M (\beta^3 + \gamma^3) \xi, \\
  h_2 &= B (\Omega_2 + \eta) + \iint \rho_1 dx dy dz (uz - wx) = B (\Omega_2 + \eta) + \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2} \Omega_2 \\
  &\quad + \frac{1}{6} M (\gamma^3 + \alpha^3) \eta, \\
  h_3 &= C (\Omega_3 + \zeta) + \iint \rho_1 dx dy dz (vx - uy) = C (\Omega_3 + \zeta) + \frac{1}{6} M \left( \frac{\alpha^2 - \beta^2}{\alpha^2 + \beta^2} \Omega_3 \right) \\
  &\quad + \frac{1}{6} M (\alpha^3 + \beta^3) \zeta
\end{align*}
\]

where

\[
\begin{align*}
  \mu &= \frac{1}{6} M (\alpha^2 - \gamma^2), & \nu &= \frac{1}{6} M (\beta^2 - \gamma^2)
\end{align*}
\]

If the system be disturbed from a motion of pure rotation, with angular velocity \( \omega \), about the axis of \( z \); \( \xi, \eta, \Omega_1, \Omega_2, \Omega_3 \) will all be small quantities, while \( \xi \) will be approximately equal to \( \omega \), and hence, on omitting small quantities of the second order and putting \( \zeta = \omega \) in small terms, the equations of angular momentum, viz.:

\[
\begin{align*}
  \dot{h}_1 - h_2 v + h_3 \xi &= 0 \\
  \dot{h}_2 - h_3 p + h_1 v &= 0 \\
  \dot{h}_3 - h_1 q + h_2 v &= 0
\end{align*}
\]

where

\[
\begin{align*}
  p &= \Omega_1 + \xi \\
  q &= \Omega_2 + \eta \\
  r &= \Omega_3 + \zeta
\end{align*}
\]
become
\[
\Lambda (\dot{\Omega}_1 + \dot{\xi}) + \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} \dot{\Omega}_1 + \frac{1}{2} M (\beta^2 + \gamma^2) \dot{\xi}
\]
\[= \left[ B (\Omega_2 + \eta) + \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2} \Omega_2 + \frac{1}{2} M (\alpha^2 + \gamma^2) \eta \right] \omega + (\Omega_2 + \eta) \left[ C + \frac{1}{2} M (\alpha^2 + \beta^2) \right] \omega = 0
\]
\[
B (\dot{\Omega}_2 + \dot{\eta}) + \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2} \dot{\Omega}_2 + \frac{1}{2} M (\gamma^2 + \alpha^2) \eta
\]
\[= (\Omega_1 + \xi) \left[ C + \frac{1}{2} M (\alpha^2 + \beta^2) \right] \omega + \left[ \Lambda (\Omega_1 + \xi) + \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} \Omega_1 + \frac{1}{2} M (\beta^2 + \gamma^2) \dot{\xi} \right] \omega = 0
\]
\[
C (\dot{\Omega}_3 + \dot{\xi}) + \frac{1}{2} M (\alpha^2 - \beta^2) \dot{\Omega}_3 + \frac{1}{2} M (\alpha^2 + \beta^2) \dot{\xi} = 0.
\]

HELMHOLTZ's equations of vortex motion are
\[
\dot{\xi} = -\frac{2\alpha^2}{\alpha^2 + \gamma^2} \omega \Omega_2, \quad \eta = \frac{2\beta^2}{\beta^2 + \gamma^2} \omega \Omega_1, \quad \dot{\xi} = 0.
\]

Hence, if we put \( \xi_1, \eta_1, \Omega_1, \Omega_2, \Omega_3, \xi - \omega \) each proportional to \( e^{\omega t} \), and introduce, for brevity, the notation \( A' \equiv \frac{1}{2} M (\beta^2 + \gamma^2), \) &c.,
\[
\begin{align*}
\lambda \frac{i}{\omega} \left[ \left( A + \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} \right) \Omega_1 + (A + A') \dot{\xi} \right] & + \left[ C + C' - B - \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2} \right] \Omega_2 + (C + C' - B - B') \eta = 0, \\
\left[ C + C' - A - \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} \right] \Omega_1 & + (C + C' - A - A') \dot{\xi} - \frac{\lambda \xi}{\omega} \left[ \left( B + \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2} \right) \Omega_2 + (B + B') \eta \right] = 0,
\end{align*}
\]
\[
\frac{\lambda \xi}{\omega} \dot{\xi} + \frac{2\alpha^2}{\alpha^2 + \gamma^2} \Omega_2 = 0, \quad \frac{\lambda \xi}{\omega} \eta - \frac{2\beta^2}{\beta^2 + \gamma^2} \Omega_1 = 0
\]
\[
\Omega_3 = 0, \quad \xi = \omega.
\]

Eliminating \( \Omega_1, \Omega_2, \xi, \eta \), the period equation is
\[
\begin{align*}
\frac{\lambda \xi}{\omega} \left[ A + \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} \right], \quad C + C' - B - \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2}, \quad \frac{\lambda \xi}{\omega} (A + A'), \quad C + C' - B - B' \\
C + C' - A - \nu \frac{\beta^2 - \gamma^2}{\beta^2 + \gamma^2} - \frac{\lambda \xi}{\omega} \left[ B + \mu \frac{\alpha^2 - \gamma^2}{\alpha^2 + \gamma^2} \right], \quad C + C' - A - A', \quad -\frac{\lambda \xi}{\omega} (B + B') \quad = 0.
\end{align*}
\]
On expanding and arranging according to powers \( \omega, \lambda \), this determinant reduces to

\[
\lambda^4 \left[ \alpha \left( \beta^2 + \gamma^2 \right) + \nu \left( \beta^2 - \gamma^2 \right) \right] \left[ B \left( \alpha^2 + \gamma^2 \right) + \mu \left( \alpha^2 - \gamma^2 \right) \right] \\
- \omega^2 \alpha^2 \left[ \left( \alpha^2 + \gamma^2 \right) \left( \beta^2 + \gamma^2 \right) \left( B - C - \nu \right) \left( A - C - \mu \right) + 4\alpha^2 \beta^2 \left( A + \nu \right) \left( B + \mu \right) \right. \\
+ 4\mu \beta^2 \gamma^2 \left( B - C - \nu \right) + 4\nu \alpha^2 \gamma^2 \left( A - C - \mu \right) \right] \\
+ \omega^4 \left[ 4\alpha^2 \beta^2 \left( B - C - \nu \right) \left( A - C - \mu \right) \right] = 0. 
\] (5).

\( \S 2. \) Case of Shell without Inertia.

If the shell be so thin that we may neglect its inertia compared with that of the fluid, we may put \( \alpha = B = C = 0 \), and equation (5) then becomes

\[
\left( \alpha^2 - \gamma^2 \right) \left( \beta^2 - \gamma^2 \right) \lambda^4 - \omega^2 \alpha^2 \left\{ \gamma^4 - 3 \left( \alpha^2 + \beta^2 \right) \gamma^2 + 5\alpha^2 \beta^2 \right\} + 4\omega^4 \alpha^2 \beta^2 = 0 \quad (6); 
\]

when the system is symmetrical about the axis of rotation \( \alpha^2 = \beta^2 \), and this equation reduces to

\[
\lambda^4 \left( \alpha^2 - \gamma^2 \right)^2 - \omega^2 \alpha^2 \left( \alpha^2 - \gamma^2 \right) \left( 5\alpha^2 - \gamma^2 \right) + 4\omega^4 \alpha^2 \beta^2 = 0, 
\]

the roots of which are

\[
\lambda^2 = \frac{\omega^2}{4} \left\{ 1 \pm \sqrt{\frac{9\alpha^2 - \gamma^2}{\alpha^2 - \gamma^2}} \right\}^2. 
\] (7)

These are the same as the values obtained by Bryan ('Phil. Trans.', 1889, A, p. 208), for the case of a spheroid whose surface is free. As is there indicated, the modes of oscillation corresponding to these periods are such that the surface of the spheroid maintains its shape, but changes its position. Such oscillations will, of course, not be affected by supposing the fluid contained in a rigid shell without inertia, and we might have expected to obtain the same values for the periods, when the figure of the shell agrees with a possible figure of equilibrium of the fluid rotating freely.

From (7) we see that the roots, if real, are positive; in order that they may be real, we require that \( 9\alpha^2 > \gamma^2 \) and \( \alpha^2 > \gamma^2 \) must have the same sign.

Hence a necessary condition for ordinary stability is

\[
\gamma^2 > 9\alpha^2 \quad \text{or} \quad \gamma^2 < \alpha^2, 
\]
i.e., \( \gamma \) must not lie between \( \alpha \) and \( 3\alpha \).

Returning to the case where \( \alpha^2 \neq \beta^2 \), in order that the roots may be real and positive, we must have

\[
(1) \quad \left( \gamma^2 - \alpha^2 \right) \left( \gamma^2 - \beta^2 \right) > 0. \\
(2) \quad \gamma^4 - 3 \left( \alpha^2 + \beta^2 \right) \gamma^2 + 5\alpha^2 \beta^2 > 0. \\
(3) \quad \left\{ \gamma^4 - 3 \left( \alpha^2 + \beta^2 \right) \gamma^2 + 5\alpha^2 \beta^2 \right\}^2 - 16\alpha^2 \beta^2 \left( \gamma^2 - \alpha^2 \right) \left( \gamma^2 - \beta^2 \right) > 0. 
\]
The 1st condition requires that $\gamma^2$ should not lie between $\alpha^2$ and $\beta^2$.

Now

$$\gamma^4 - 3(\alpha^2 + \beta^2)\gamma^2 + 5\alpha^2\beta^2 = (\gamma^2 - 3\alpha^2)(\gamma^2 - 3\beta^2) - 4\alpha^2\beta^2$$

$$= (3\alpha^2 - \gamma^2)(3\beta^2 - \gamma^2) - 4\alpha^2\beta^2.$$

The 1st form shows that condition (2) is certainly satisfied if

$$\gamma^2 > 5\alpha^2 \quad \text{and also} \quad > 5\beta^2.$$ 

The 2nd shows that it is satisfied if $\gamma^2 < \alpha^2$ and $< \beta^2$.

Lastly,

$$\begin{align*}
\{\gamma^4 - 3(\alpha^2 + \beta^2)\gamma^2 + 5\alpha^2\beta^2\}^2 - 16\alpha^2\beta^2(\gamma^2 - \alpha^2)(\gamma^2 - \beta^2) \\
= (\gamma^2 - \alpha^2)(\gamma^2 - \beta^2)\{\gamma^4 - 5(\alpha^2 + \beta^2)\gamma^2 + 9\alpha^2\beta^2\} + 4(\alpha^2 - \beta^2)^2\gamma^4
\end{align*}$$

\[
\begin{cases}
(\gamma^2 - \alpha^2)(\gamma^2 - \beta^2)\{\gamma^4 - 5\alpha^2(\gamma^2 - 5\beta^2) - 16\alpha^2\beta^2\} + 4(\alpha^2 - \beta^2)^2\gamma^4 \\
(\alpha^2 - \gamma^2)(\beta^2 - \gamma^2)\{5\alpha^2 - \gamma^2\}(5\beta^2 - \gamma^2) - 16\alpha^2\beta^2\} + 4(\alpha^2 - \beta^2)^2\gamma^4.
\end{cases}
\]

Hence condition (3) will certainly be satisfied if $\gamma^2 > 9\alpha^2$ and also $> 9\beta^2$, or if $\gamma^2 < \alpha^2$ and also $< \beta^2$.

Thus the roots of (6) will both be real and positive if

$$\gamma < \alpha \quad \text{and also} \quad < \beta,$$

or if

$$\gamma > 3\alpha \quad \text{and also} \quad > 3\beta.$$

These conditions are sufficient, but not necessary, to ensure stability; the necessary conditions are given by the inequalities (1), (2), (3).

The analytical conditions here discussed are approximately realised in the case of a liquid gyrostat (vide 'Nature,' vol. 15, p. 297) mounted on gimbals in such a way that the centre of gravity is held at rest. The inertia of the gimbals will be unimportant when the rotation is rapid, and, if we may also neglect the inertia of the case compared with that of the fluid, the gyrostat will be stable when set rotating about its least axis; it will also be stable when set rotating about its greatest axis when this axis is, at least, three times as great as either of the others. It will, however, certainly be unstable when set rotating about its mean axis.

§ 3. Approximate Solution of the Period Equation.

Let us for the future suppose that the cavity which contains fluid is approximately spherical, so that $\frac{\alpha - \gamma}{\gamma}, \frac{\beta - \gamma}{\gamma}$ are small quantities.
Suppose
\[ \frac{\alpha - \gamma}{\gamma} = \epsilon_1, \quad \frac{\beta - \gamma}{\gamma} = \epsilon_2. \]

From (3) we have
\[ \nu (\alpha^2 - \gamma^2) = \mu (\beta^2 - \gamma^2); \]
therefore, if we neglect squares of \( \epsilon_1, \epsilon_2 \),
\[ \frac{\mu}{\epsilon_1} = \frac{\nu}{\epsilon_2} = qC \text{ say.} \]

In the case where the thickness of the shell is finite compared with its linear dimensions \( q \) will be a finite quantity; when the shell is thin \( q \) will be large, and when the fluid nucleus is small compared with the dimensions of the whole system \( q \) will be small, the densities of the fluid and of the crust being supposed comparable with one another. In all cases \( q \) will be positive.

If \( \epsilon_1, \epsilon_2 \) are each equal to zero, the equation (5) becomes
\[ AB\lambda^4 - [(C - A)(C - B) + AB] \lambda^2 \omega^2 + (C - A)(C - B) \omega^4 = 0, \]

or
\[ (\lambda^2 - \omega^2)[AB\lambda^2 - (C - A)(C - B) \omega^2] = 0. \]

Thus we obtain as a first approximation to the roots
\[ \lambda^2 = \omega^2, \quad \lambda^2 = \frac{(C - A)(C - B)}{AB} \omega^2. \]

Next let us retain first powers of \( \epsilon_1, \epsilon_2 \) in (5); this equation then becomes
\[ \lambda^4 AB (1 + \epsilon_1 + \epsilon_2) \]
\[ - \omega^2 \lambda^2 [(C - A)(C - B)(1 + \epsilon_1 + \epsilon_2) + AB (1 + 2\epsilon_1 + 2\epsilon_2) + q (AC\epsilon_1 + BC\epsilon_2)] \]
\[ + \omega^4 (1 + 2\epsilon_1 + 2\epsilon_2) (C - A + qC\epsilon_1)(C - B + qC\epsilon_2) = 0, \]

or
\[ (\lambda^2 - \omega^2) (AB\lambda^2 - C - A C - B \omega^2) \]
\[ + \epsilon_1 [AB\lambda^4 - \omega^2 \lambda^2 ((C - A)(C - B) + 2AB + qAC) \]
\[ + \omega^4 (C - B) \{2(C - A) + qC\}] \]
\[ + \epsilon_2 [AB\lambda^4 - \omega^2 \lambda^2 ((C - A)(C - B) + 2AB + qBC) \]
\[ + \omega^4 (C - A) \{2(C - B) + qC\}] = 0 \quad (8); \]

dividing by \( AB\lambda^2 - (C - A)(C - B) \omega^2 \), and putting \( \lambda^2 = \omega^2 \) in the terms which contain \( \epsilon_1 \) or \( \epsilon_2 \) as a factor, we obtain as a closer approximation to the root \( \lambda^2 = \omega^2 \),
\[ 3 \rho 2 \]
\[ \lambda^2 = \omega^2 \left[ 1 - \epsilon_1 \left\{ \frac{(C - A)(C - B) - AB + qC(C - B - A)}{AB - (C - A)(C - B)} \right\} \\
- \epsilon_2 \left\{ \frac{(C - A)(C - B) - AB + qC(C - B - A)}{AB - (C - A)(C - B)} \right\} \right] = \omega^2 \left[ 1 + (\epsilon_1 + \epsilon_2)(1 + q) \right] = \omega^2 (1 + 2E) \text{ say} \ldots \ldots \ldots \ldots \llap{\text{(9),}} \]

therefore

\[ \lambda = \pm \omega (1 + E). \]

Again, dividing by \( \lambda^2 - \omega^2 \) in (8), and putting \( \lambda^2 = \frac{(C - A)(C - B)}{AB} \omega^2 \) in the small terms, an approximate value of the second root, correct to first powers of \( \epsilon_1, \epsilon_2 \), is given by

\[ AB\lambda^2 - (C - A)(C - B) \omega^2 = - \epsilon_1 \omega^2 \frac{qC(C - B) - qAC(C - A)(C - B)}{AB} - 1 \]

\[ - \epsilon_2 \omega^2 \frac{qC(C - A) - qBC(C - A)(C - B)}{AB} - 1, \]

or

\[ \lambda^2 = \omega^2 \left[ \frac{(C - A)(C - B)}{AB} + \epsilon_1 q \frac{C - B}{B} + \epsilon_2 q \frac{C - A}{A} \right] \]

\[ = \omega^2 \left[ \frac{C - A}{A} + \epsilon_1 q \left\{ \frac{C - B}{B} + \epsilon_2 q \right\} \right] \ldots \ldots \ldots \ldots \llap{\text{(10)}} \]

to the same order of approximation.

This approximation involves the assumption that \( \epsilon_1, \epsilon_2 \) are small compared with \( \frac{C - A}{A}, \frac{C - B}{B} \); the approximate value of the root will, however, be the same if we suppose \( \frac{C - A}{A}, \frac{C - B}{B} \) to be small quantities of the same order as \( \epsilon_1, \epsilon_2 \).

Let us put

\[ \frac{C - A}{A} = \kappa_1, \quad \frac{C - B}{B} = \kappa_2. \]

Retaining only finite terms in (5), we obtain as a first approximation to the roots \( \lambda^2 = \omega^2 \) and \( \lambda^2 = 0 \); also, the independent term in (5) is a small quantity of the second order in \( \kappa_1, \kappa_2, \epsilon_1, \epsilon_2 \). Thus the root which approximates to \( \lambda^2 = 0 \) will be of the second order. Regarding \( \lambda^2 \) as of the second order, and retaining only terms of this order in (5), we get

\[ \lambda^2 \left[ 4AB\omega^2 \beta^2 \right] - \omega^4 \cdot 4a^2 \beta^2 \left\{ B\kappa_2 + qC\epsilon_3 \right\} \left\{ A\kappa_1 + qC\epsilon_1 \right\} = 0, \]
\[ \lambda^2 = \omega^2 \cdot \left( \kappa_1 + q \frac{C}{A} \epsilon_1 \right) \left( \kappa_2 + q \frac{C}{B} \epsilon_2 \right) = \omega^2 \cdot (\kappa_1 + q\epsilon_1) (\kappa_2 + q\epsilon_2) \]

to the same order, and this is the value obtained above (10).

§ 4. Application to the Case of the Earth.

The nature of the two types of oscillation will be found fully discussed in the Appendix. It is there shown that the oscillation corresponding to the root \( \omega (1 + E) \) is that previously examined by Hopkins in his 'Researches in Physical Geology,' whereas the second type is analogous to the motion of a rigid body when disturbed from a motion of rotation about a principal axis.

If the Earth could be regarded as a system such as we have been considering, we see that in addition to the ordinary Solar and Lunar Nutations, which would be of the same nature as when the Earth is supposed solid throughout, there might exist certain free nutations the amplitude of which could only be determined by observation. If the amplitudes were sufficiently large, the oscillations corresponding to the root \( \lambda = \omega (1 + E) \) would render themselves visible in the same way as the Solar and Lunar Nutations, namely, by small periodic displacements common to all stars. The period of these displacements would be \( 1/E \) sidereal days, and a knowledge of it would enable us to determine \( E \), a quantity which depends on the form of the internal surface and the thickness of the crust.

The oscillations which correspond to the root \( \lambda = \omega \sqrt{[(\kappa_1 + q\epsilon_1) (\kappa_2 + q\epsilon_2)]} \) would manifest themselves in a different manner. They are, in fact, similar to the "Eulerian" nutation (vide Tisserand, 'Mécanique Céleste,' vol. 2, p. 494), and will involve a small periodic change in the latitude of places on the Earth's surface, as found by meridian observations of a circumpolar star, this change taking place in a period of \( \{(\kappa_1 + q\epsilon_1) (\kappa_2 + q\epsilon_2)\}^{-1} \) sidereal days.

Now it appears probable that in oscillations of long period, such as Precession, the effects of fluid friction would be to make the internal fluid move with the crust as if rigidly connected to it (Tisserand, 'Mécanique Céleste,' vol. 2, p. 480, or Lord Kelvin, 'Popular Lectures and Addresses,' vol. 2, p. 244). Hence, if \( \mathbf{A}, \mathbf{A}, \mathbf{C} \) be the principal moments of inertia for the Earth as a whole, supposed symmetrical about its axis of rotation, the Theory of Precession will still enable us to determine the value of \( \frac{\mathbf{C} - \mathbf{A}}{\mathbf{C}} \), as \( \frac{1}{305} \).

But, if we put \( \kappa_2 = \kappa_1, \epsilon_3 = \epsilon_1 \), and denote by \( M \) the mass of the fluid,

\[ \mathbf{C} = C + \frac{3}{2} M a^2 = C \{1 + q (1 + 2\epsilon_1)\}, \]
\[ \mathbf{A} = A + \frac{1}{3} M (a^2 + v^2) = A + q C (1 + \epsilon_1). \]
Therefore,
\[
\frac{C - A}{C} = \frac{C - A + gC_{e_1}}{C(1 + q + 2ge_1)} = \frac{\kappa_1 + ge_1}{1 + q}
\]
very nearly.

Therefore the period in which the latitude variations will take place is
\[
\frac{1}{\kappa_1 + ge_1} \text{ sidereal days} = \frac{C}{C - A} \cdot \frac{1}{1 + q} \text{ sidereal days};
\]
when the Earth is supposed solid throughout, this period is
\[
\frac{C}{C - A} \text{ sidereal days.}
\]

We thus see that if the Earth consisted of a rigid shell containing a homogeneous fluid nucleus, the theoretical period of 365 days, calculated on the assumption of the Earth’s rigidity throughout, would be diminished in the ratio \(1 : 1 + q\), where \(q\) is an essentially positive quantity, whose magnitude increases with the size of the nucleus.

In order to form some idea of the magnitude of this effect, let us suppose that the fluid and the crust have the same density \(\rho\), and that \(r, r_1\) are the mean radii of the fluid nucleus, and of the Earth as a whole.

We then have approximately
\[
\mu = \nu = \frac{8}{15} \pi \rho r^3 e_1 \quad \text{and} \quad C = \frac{8}{15} \pi \rho (r_1^3 - r^3).
\]

Therefore,
\[
q = \frac{\mu}{\epsilon_1 C} = \frac{r^3}{r_1^3 - r^3},
\]

\[
1 + q = \frac{r_1^3}{r_1^3 - r^3}, \quad \frac{1}{1 + q} = 1 - \left(\frac{r}{r_1}\right)^3,
\]
and the period will be diminished by \(\left(\frac{r}{r_1}\right)^3 \times 305\) days.

Taking the mean radius of the Earth as 4000 miles, we obtain the following table, where the first line gives the thickness of the crust in miles, and the second the diminution of the period in sidereal days:

<table>
<thead>
<tr>
<th>Thickness of crust in miles</th>
<th>2000</th>
<th>1000</th>
<th>500</th>
<th>250</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diminution of period in days</td>
<td>5</td>
<td>21</td>
<td>156</td>
<td>221</td>
<td>269</td>
</tr>
</tbody>
</table>
ROTATING ELLIPSOIDAL SHELL CONTAINING FLUID.

Now, although in the light of Professor Newcomb's work ('Astron. Soc. Monthly Notices,' March, 1892), it appears probable that this effect would be modified by the elasticity of the Crust, it could scarcely be reversed if the fluid nucleus were of any considerable extent. We must, therefore, conclude that the observations on latitude-variation, so far from establishing the existence of a fluid interior, as supposed by M. Folie, rather tend to confirm the views hitherto maintained by physicists on other grounds, that there can be no internal fluid mass of any considerable extent.

APPENDIX.

TREATMENT OF THE PROBLEM BY LAMÉ ANALYSIS.

§ 1. Equations of Motion of Fluid.

Let us refer to rectangular axes rotating with angular velocity \( \omega \) about the axis of \( z \). The fluid is supposed to have no motion relatively to these axes other than that due to the small oscillations with which we are dealing.

Let \( u, v, w \), be the velocity-components at any point \( x, y, z \) relatively to these axes: we shall, as is usual in small-oscillation problems, neglect squares and products of the small quantities \( u, v, w \).

The actual velocity-components parallel to the instantaneous positions of the moving axes will be

\[
  u - \omega y, \quad v + \omega x, \quad w,
\]

and the differential equations of motion of the fluid are therefore (Basset, 'Hydrodynamics,' p. 22)

\[
\begin{align*}
  \frac{\partial v}{\partial t} - \omega (v + \omega x) - \omega v &= \frac{\partial}{\partial x} \left( V_1 - \frac{p}{\rho_1} \right), \\
  \frac{\partial x}{\partial t} + \omega (u - \omega y) + \omega u &= \frac{\partial}{\partial y} \left( V_1 - \frac{p}{\rho_1} \right), \\
  \frac{\partial w}{\partial t} &= \frac{\partial}{\partial z} \left( V_1 - \frac{p}{\rho_1} \right),
\end{align*}
\]

where \( V_1 \) is the gravitation-potential of the forces to which the fluid is subject, \( p \) the fluid-pressure, and \( \rho_1 \) the density.

Putting

\[
  \psi = V_1 - 1 = \frac{p}{\rho_1} = \frac{1}{2} \omega \left( x^2 + y^2 \right)
\]

the above equations reduce to

\[
\begin{align*}
  \frac{\partial u}{\partial t} - 2\omega v &= \frac{\partial \psi}{\partial x} \\
  \frac{\partial v}{\partial t} + 2\omega u &= \frac{\partial \psi}{\partial y} \\
  \frac{\partial w}{\partial t} &= \frac{\partial \psi}{\partial z}
\end{align*}
\]

.......

(1)

(2)
We have, in addition, the equation of continuity

\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \]  

(3).

Equations (2), (3) are sufficient to determine \( u, v, w, \psi \), subject to certain boundary conditions.

From (2) we obtain

\[
\begin{bmatrix}
\frac{\partial^2}{\partial t^2} + 4\omega^2 & u = \frac{\partial^2 \psi}{\partial x^2} + 2\omega \frac{\partial \psi}{\partial y} \\
\frac{\partial^2}{\partial t^2} + 4\omega^2 & v = \frac{\partial^2 \psi}{\partial y^2} - 2\omega \frac{\partial \psi}{\partial x} \\
\frac{\partial^2}{\partial t^2} & = \frac{\partial^4 \psi}{\partial z^2}
\end{bmatrix}
\]  

(4).

Applying the operators \( \partial / \partial x, \partial / \partial y, \partial / \partial z \), and adding, we obtain by means of (3)

\[ -4\omega^3 \frac{\partial \psi}{\partial z} = \frac{\partial}{\partial t} (\nabla^2 \psi) \], where \( \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \),

or, by the third of equations (2),

\[ 4\omega^3 \frac{\partial^2 \psi}{\partial t^2} + \frac{\partial^2}{\partial t^2} (\nabla^2 \psi) = 0 \]  

(5).

This is Poindcaré's differential equation for the oscillations of a mass of fluid about a steady motion of pure rotation.

Let us now suppose that the system is executing one of its component harmonic vibrations.

Assume that

\[ u = u_1 e^{i\lambda t}, \quad v = v_1 e^{i\lambda t}, \quad w = w_1 e^{i\lambda t}; \]

and

\[ \psi = \psi_1 e^{i\lambda t}. \]

Putting these values in (4), (5), and dividing out by the time factor, we get

\[
\begin{align*}
u_1 &= \frac{1}{4\omega^2 - \lambda^2} \left\{ i \lambda \frac{\partial \psi_1}{\partial x} + 2\omega \frac{\partial \psi_1}{\partial y} \right\} \\
w_1 &= \frac{1}{4\omega^2 - \lambda^2} \left\{ i \lambda \frac{\partial \psi_1}{\partial y} - 2\omega \frac{\partial \psi_1}{\partial x} \right\}
\end{align*}
\]  

(6),

while \( \psi_1 \) satisfies the equation

\[ \frac{\partial^2 \psi_1}{\partial x^2} + \frac{\partial^2 \psi_1}{\partial y^2} + \left( 1 - \frac{4\omega^2}{\lambda^2} \right) \frac{\partial^2 \psi_1}{\partial z^2} = 0 \]  

(7).
§ 2. The Boundary Conditions.

The position of the shell at any instant may be defined by means of three coordinates, \( \theta_1, \theta_2, \theta_3 \), which denote the small angular displacements, about the axes of reference, of the shell from the position it would occupy in the steady motion.

The displacements parallel to the coordinate axes of the point of the shell, whose coordinates are \((x, y, z)\), are

\[-y\theta_3 + z\theta_2, \quad -z\theta_1 + x\theta_3, \quad -x\theta_2 + y\theta_1.\]

If \( \cos \alpha, \cos \beta, \cos \gamma \) be the direction cosines of the normal to the undisturbed surface, the normal distance between this surface and the displaced surface will be

\[-y\theta_3 + z\theta_2 \cos \alpha + (-z\theta_1 + x\theta_3) \cos \beta + (-x\theta_2 + y\theta_1) \cos \gamma = \theta_1 (y \cos \gamma - z \cos \beta) + \theta_2 (z \cos \alpha - x \cos \gamma) + \theta_3 (x \cos \beta - y \cos \alpha).\]

The condition to be satisfied at the boundary is that the rate of increase of this length must be equal to the component velocity of the fluid, relative to the moving axes, in the direction of the normal to the undisturbed surface. Now as these relative velocities are all small quantities whose squares we are neglecting, it is unnecessary to distinguish between the velocities at the disturbed and undisturbed surfaces; thus, at the latter surface we require

\[u \cos \alpha + v \cos \beta + w \cos \gamma = \dot{\theta}_1 (y \cos \gamma - z \cos \beta) + \dot{\theta}_2 (z \cos \alpha - x \cos \gamma) + \dot{\theta}_3 (x \cos \beta - y \cos \alpha).\]

Putting \( \dot{\theta}_1 = \theta_1 e^{\lambda t}, \dot{\theta}_2, \dot{\theta}_3 \), and omitting the exponential factor, we obtain

\[u_1 \cos \alpha + v_1 \cos \beta + w_1 \cos \gamma = i\lambda [\theta'_{1} (y \cos \gamma - z \cos \beta) + \theta'_{2} (z \cos \alpha - x \cos \gamma) + \theta'_{3} (x \cos \beta - y \cos \alpha)].\]

or, putting in the values of \( u_1, v_1, w_1, \psi_1 \) from (6),

\[\frac{\lambda}{4\omega^2 - \lambda^2} \left\{ \frac{\partial \psi_1}{\partial x} \cos \alpha + \frac{\partial \psi_1}{\partial y} \cos \beta + \frac{\partial \psi_1}{\partial z} \cos \gamma \left( 1 - \frac{4\omega^2}{\lambda^2} \right) \right\} \]

\[-\frac{2\omega i}{4\omega^2 - \lambda^2} \left\{ \frac{\partial \psi_1}{\partial y} \cos \alpha - \frac{\partial \psi_1}{\partial x} \cos \beta \right\} \]

\[= \lambda [\theta'_1 (y \cos \gamma - z \cos \beta) + \theta'_2 (z \cos \alpha - x \cos \gamma) + \theta'_3 (x \cos \beta - y \cos \alpha)].\]

Let us now put

\[1 - \frac{4\omega^2}{\lambda^2} = r^2, \quad z = rz'.\]
Corresponding to any series of points whose coordinates are denoted by \((x, y, z)\), we shall obtain a new series whose coordinates are \((x, y, z')\), which will be real or imaginary according as \(\lambda^2\) is greater or less than \(4\omega^2\). We will take as the standard case that in which \(\lambda^2 > 4\omega^2\).

If the point \((x, y, z)\) trace out any surface whose equation is \(f(x, y, z) = 0\), the corresponding point \((x, y, z')\) will trace out a new surface whose equation is \(f'(x, y, z') = 0\). The part of this latter surface which corresponds to the real part of the surface \(f(x, y, z) = 0\) will, however, be purely imaginary if \(\lambda^2 < 4\omega^2\).

If \((\cos \alpha, \cos \beta, \cos \gamma)\), \((\cos \alpha', \cos \beta', \cos \gamma')\) be the direction-cosines of the normals to the two surfaces, we have

\[
\cos \alpha' : \cos \beta' : \cos \gamma' = \frac{\partial f}{\partial x} : \frac{\partial f}{\partial y} : \frac{\partial f}{\partial z'} = \frac{\partial f}{\partial x} : \frac{\partial f}{\partial y} : \tau \left(\frac{\partial f}{\partial z}\right) = \cos \alpha : \cos \beta : \tau \cos \gamma.
\]

Substituting in equations (7), (8), the differential equation for \(\psi_1\) takes the form

\[
\frac{\partial^2 \psi_1}{\partial x^2} + \frac{\partial^2 \psi_1}{\partial y^2} + \frac{\partial^2 \psi_1}{\partial z'^2} = 0 \quad \ldots \ldots \ldots \ldots \quad (9),
\]

while if \(f(x, y, z) = 0\) be the equation to the undisturbed boundary of the fluid, \(\psi_1\) must satisfy the equation

\[
\lambda \left[ \frac{\partial \psi_1}{\partial x} \cos \alpha' + \frac{\partial \psi_1}{\partial y} \cos \beta' + \frac{\partial \psi_1}{\partial z} \cos \gamma' \right] - 2\omega i \left[ \frac{\partial \psi_1}{\partial y} \cos \alpha' - \frac{\partial \psi_1}{\partial x} \cos \beta' \right] = (4\omega^2 - \lambda^2) \lambda \left[ \begin{array}{c}
\theta_1 \left(\frac{y}{\tau} \cos \gamma' - \tau' \cos \beta'\right) + \theta_2 \left(\tau' \cos \alpha' - \frac{x}{\tau} \cos \gamma'\right) + \theta_3 \left(x \cos \beta' - y \cos \alpha'\right)
\end{array} \right] \quad \ldots \ldots \ldots \ldots \quad (10)
\]

at the surface \(f(x, y, z') = 0\).

The problem of finding the motion of the fluid is thus reduced to that of obtaining solutions of equation (9) consistent with the boundary condition (10) at the surface \(f(x, y, \tau z') = 0\).

\[\text{§ 3. Case of Ellipsoidal Surface.}\]

Hitherto, no assumption has been made as to the form of the surface of the fluid. Let us now suppose that it is given by the equation

\[
\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (A),
\]
that is to say, that it is an ellipsoid whose principal axes coincide with the axes of reference.

We will take as the standard case, that in which

\[ \rho^2 > c^2 > b^2 > 0. \]

Put

\[ \rho^2 - c^2 = (\rho^2 - c^2) \tau^2. \]

The equation to the auxiliary surface \( f(x, y, \tau') = 0 \) becomes

\[ \frac{x^2}{\rho^2} + \frac{y^2}{\rho^2 - b^2} + \frac{z'^2}{\rho^2 - c^2} = 1 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (A'). \]

Let us now introduce two sets of elliptic coordinates \((\rho, \mu, \nu)\), \((\rho', \mu', \nu')\), connected with \((x, y, z)\) \((x, y, z')\) respectively by the equations

\[
\begin{align*}
\frac{x}{\rho} &= \frac{\mu \nu}{bc^2} \frac{y}{\sqrt{(\rho^2 - b^2)}} = \frac{\sqrt{(\mu^2 - b^2)(\mu^2 - b^2)}}{b \sqrt{(\rho^2 - b^2)}}, \\
\frac{y}{\rho} &= \frac{\mu' \nu'}{bc'} \frac{y}{\sqrt{(\rho'^2 - b^2)}} = \frac{\sqrt{(\mu'^2 - b^2)(\mu'^2 - b^2)}}{b' \sqrt{(\rho'^2 - b^2)}}, \\
\frac{z}{\rho^2 - c^2} &= \frac{\nu}{\sqrt{c^2 - b^2}} \frac{z}{b \sqrt{(c^2 - b^2)}}, \\
\frac{z'}{\rho^2 - c^2} &= \frac{\nu'}{\sqrt{c'^2 - b'^2}} \frac{z'}{b' \sqrt{(c'^2 - b'^2)}}.
\end{align*}
\]

\( \rho' \) will be equal to \( \rho \) for points which lie on the surfaces \((A)\) \((A')\), but not otherwise.

Let us also put

\[
X = x/\rho, \quad Y = y/\sqrt{(\rho^2 - b^2)}, \quad Z = z/\sqrt{(\rho^2 - c^2)} = z'/\sqrt{(\rho'^2 - c'^2)}, \quad (13)
\]

for points on these surfaces; so that \(X, Y, Z\) are subject to the relation

\[ X^2 + Y^2 + Z^2 = 1 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (B). \]

\(X, Y, Z\) may therefore be regarded as the coordinates of a point lying on a sphere of unit radius.

Denote by \(R, M, N\) three conjugate Lamé functions of the elliptic coordinates \(\rho, \mu, \nu\), and by \(R', M', N'\) three similar functions of the coordinates \(\rho', \mu', \nu'\).

A form of solution of equation (9) convenient for satisfying boundary conditions at the surface \((A')\) is

\[ \psi_i = \Sigma A'R'M'N' \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (14). \]

The effect of the fluid on the motion of the shell will depend only on the fluid pressure over the surface, and this by (1) will involve the value of \(\psi_i \) at the surface.
To find the value of $\psi_1$ at the surface (A), we may transform the expression (14) for $\psi_1$ first to the surface (B) and then from (B) to (A).

Now, by a known property of Lamé products (vide Heine, 'Kugelfunctionen,' vol. 1, § 89), if $M$, $N$ be two conjugate functions of order $n$, the product $MN$ at the surface (A) will transform into a surface harmonic of order $n$ at the surface (B); and, conversely, any surface harmonic of order $n$ at the surface (B), when transformed to the surface (A), can be expanded in a series consisting of Lamé products with constant coefficients, each of which products will be of the $n$th order.

The same conclusions will hold for the surface (A') and the sphere (B).

We can thus express the value of $\psi_1$ at the surface (A) in terms of a series of Lamé products, in which each term will be of the same order as that from which it arises in (14).

The couples on the shell due to fluid pressure are

$$\iint p \, d\sigma (y \cos \gamma - z \cos \beta), \quad \iint p \, d\sigma (z \cos \gamma - x \cos \beta), \quad \iint p \, d\sigma (x \cos \beta - y \cos \gamma),$$

where $d\sigma$ is an element of the surface and the integrals are taken over the whole surface.

If $P$ denote the perpendicular from the centre on the tangent plane to the ellipsoid (A) and $l = \frac{P}{\rho \sqrt{(\rho^2 - b^2)(\rho^2 - c^2)}}$

$$y \cos \gamma - z \cos \beta = Pyz \left\{ \frac{1}{\rho^2 - c^2} - \frac{1}{\rho^2 - b^2} \right\} = \frac{Pyz (c^2 - b^2)}{(\rho^2 - c^2)(\rho^2 - b^2)},$$

and $Pyz$ is proportional to

$$l\sqrt{(\mu^2 - b^2)(c^2 - \mu^2)} \sqrt{(b^2 - \nu^2)(c^2 - \nu^2)} = lM_1N_1,$$

where $M_1$, $N_1$ are two conjugate Lamé functions of the second order. But, if $MN$ be any two conjugate Lamé functions different from $M_1N_1$, $\iint MNN_1 d\sigma = 0$. For, if we transform to the surface of the sphere (B), $l \, d\sigma$ is equal to the corresponding element of the spherical surface, and $MN$, $M_1N_1$ transform into two different surface harmonics.

Thus the only term in $\psi_1$ which can give rise to any couple about the axis of $x$ will be the term involving the Lamé product $M_1N_1$.

Similarly the terms which can give rise to couples about the other axes will be of the second order. These, as we have seen above, all arise from terms of the second order in (14), and, in order to evaluate these couples, it will be unnecessary for us to calculate any coefficients in $\psi_1$ other than those of terms of the second order.
§ 4. Transformation of Boundary Equations.

Let us now transform our boundary conditions to the surface of the sphere (B).

We can at once express the right-hand member of equation (10) in terms of \( X, Y, Z \); for

\[
\cos \alpha' = \frac{P'_x}{\rho^2} = \frac{P'X}{\rho},
\]

\[
\cos \beta' = \frac{P'_y}{\rho^2 - \rho^2} = \frac{P'Y}{\sqrt{(\rho^2 - \rho^2)}},
\]

\[
\cos \gamma' = \frac{P'_z}{\rho^2 - \rho^2} = \frac{P'Z}{\sqrt{(\rho^2 - \rho^2)}},
\]

where \( P' \) has the same signification with reference to the ellipsoid (A') as \( P \) has with reference to the ellipsoid (A).

The right-hand member therefore becomes

\[
- \lambda^2 \tau^2 P'. \left[ \theta'_1 \frac{e^2 - b^2}{\sqrt{(\rho^2 - b^2)(\rho^2 - e^2)}} YZ + \theta'_2 \frac{(-e^2)}{\rho \sqrt{(\rho^2 - e^2)}} ZX + \theta'_3 \frac{b^2}{\rho \sqrt{(\rho^2 - b^2)}} XY \right] (15).
\]

Consider next a single term of order \( n \) in \( \psi_1 \), say \( \psi_1 = R'M'N' \). We have seen that \( M'N' \) is expressible in the form \( \epsilon S_n \), where \( \epsilon \) is some quantity which does not vary over the surface of the sphere (B) and \( S_n \) is a spherical harmonic function of degree \( n \) in \( X, Y, Z \).

If \( dn' \) denote an element of the normal to the surface (A'), we have \( P' \, dn' = \rho' \, dp' \), and therefore,

\[
\frac{\partial \psi_1}{\partial x} \cos \alpha' + \frac{\partial \psi_1}{\partial y} \cos \beta' + \frac{\partial \psi_1}{\partial z} \cos \gamma' = \frac{\partial \psi_1}{\partial n'} = \frac{P'}{\rho'} \frac{\partial \psi_1}{\partial \rho}.
\]

Now \( M', N' \) are independent of \( \rho' \). Therefore, when \( \psi_1 = R'M'N' \),

\[
\frac{\partial \psi_1}{\partial x} \cos \alpha' + \frac{\partial \psi_1}{\partial y} \cos \beta' + \frac{\partial \psi_1}{\partial z} \cos \gamma' = \frac{P'}{\rho'} \frac{\partial R'}{\partial \rho} M'N' = \frac{P'}{\rho'} \frac{\partial R'}{\partial \rho} \epsilon S_n \quad (16).
\]

Next let \( ds \) be an element of a line through \((x, y, z')\) whose direction-cosines are \((-\cos \beta', \cos \alpha', 0)\), and which, therefore, lies in the surface (A').

Then

\[
\frac{\partial \psi_1}{\partial y} \cos \alpha' - \frac{\partial \psi_1}{\partial x} \cos \beta' = \sin \gamma \frac{\partial \psi_1}{\partial s},
\]

and when \( \psi_1 = R'M'N' = R' \epsilon S_n \),

\[
\frac{\partial \psi_1}{\partial s} = \frac{\partial}{\partial s} (R' \epsilon) \cdot S_n + R' \epsilon \frac{\partial S_n}{\partial s} \quad (17).
\]
Now, the element $ds$ lies entirely in the surface $(A')$, and corresponding to every point of it there will be a point $X, Y, Z$ which lies on the sphere $(B)$. Hence, as $R', \epsilon$ do not vary over the surface of the sphere, they will remain constant as we pass along the element $ds$. Thus we have

$$\frac{\partial}{\partial s} (R' \epsilon) = 0;$$

and, therefore, from (17)

$$\frac{\partial \Phi_1}{\partial s} = R' \epsilon \cdot \frac{\partial S_a}{\partial s} = R' \epsilon \left\{ \frac{\partial S_a}{\partial X} \cdot \frac{\partial X}{\partial s} + \frac{\partial S_a}{\partial Y} \cdot \frac{\partial Y}{\partial s} + \frac{\partial S_a}{\partial Z} \cdot \frac{\partial Z}{\partial s} \right\}.$$

But from (13) we see that

$$\frac{\partial X}{\partial s} = \frac{\partial \psi}{\partial \varphi} = \frac{1}{\rho} \frac{\partial \psi}{\partial s} = \frac{1}{\rho} \left( \frac{-\cos \beta'}{\sin \gamma'} \right) = - \frac{P'\gamma}{\rho (\rho^2 - \rho^2)} \cosec \gamma' = - \frac{P'\gamma}{\rho \sqrt{(\rho^2 - \rho^2)} \cosec \gamma'}$$

$$\frac{\partial Y}{\partial s} = \frac{1}{\sqrt{(\rho^2 - \rho^2)}} \frac{\partial \psi}{\partial s} = \frac{1}{\sqrt{(\rho^2 - \rho^2)}} \left( \frac{\cos \alpha'}{\sin \gamma'} \right) = \frac{P'\gamma}{\rho \sqrt{(\rho^2 - \rho^2)} \cosec \gamma'}$$

$$\frac{\partial Z}{\partial s} = \frac{1}{\sqrt{(\rho^2 - \rho^2)}} \frac{\partial \psi}{\partial s} = 0.$$

Therefore,

$$\frac{\partial \Phi_1}{\partial s} = \frac{P' \epsilon}{\rho \sqrt{(\rho^2 - \rho^2)}} \left\{ X \frac{\partial S_a}{\partial Y} - Y \frac{\partial S_a}{\partial X} \right\} \cosec \gamma',$$

and

$$\frac{\partial \Phi_1}{\partial \varphi} \cos \alpha' - \frac{\partial \Phi_1}{\partial \varphi} \cos \beta' = \sin \gamma \frac{\partial \Phi_1}{\partial s} = \frac{P' \epsilon}{\rho \sqrt{(\rho^2 - \rho^2)}} \left\{ X \frac{\partial S_a}{\partial Y} - Y \frac{\partial S_a}{\partial X} \right\}.$$

From (15), (16), (18) we see that the boundary equation, on the assumption of the form (14) for $\psi_1$, takes the form

$$\lambda \left\{ \sum A' \frac{\partial R'}{\partial \varphi} \right\} - 2 \omega i \left\{ \sum A' \frac{R'}{\rho} \left( X \frac{\partial S_a}{\partial Y} - Y \frac{\partial S_a}{\partial X} \right) \right\}$$

$$= \lambda \lambda^2 \left\{ \theta_1' \frac{\rho (\rho^2 - \rho^2)}{\sqrt{(\rho^2 - \rho^2)} \sqrt{(\rho^2 - \rho^2)}} \frac{\partial Z}{\partial s} + \theta_2' \frac{(-\rho)}{\sqrt{(\rho^2 - \rho^2)} \sqrt{(\rho^2 - \rho^2)}} \frac{\partial X}{\partial s} + \theta_3' \frac{\rho^2}{\sqrt{(\rho^2 - \rho^2)} \sqrt{(\rho^2 - \rho^2)}} \frac{\partial Y}{\partial s} \right\}.$$
Omitting for the present the terms of the second order, if we equate to zero the coefficients of the $2n + 1$ independent harmonics, we shall obtain a series of $2n + 1$ linear equations connecting the $2n + 1$ quantities $A'$ which occur with Lamé products of order $n$. These equations show that all the quantities $A'$ vanish except for certain values of $\lambda$ which satisfy the determinantal equation obtained by eliminating them. The roots of this equation will determine the possible periods of free oscillation, and when the system is oscillating in the mode corresponding to any one of these roots, Lamé products of one order ($n$) only will appear in $\psi_1$.

These modes of oscillation do not involve any motion of the shell, and it is evident that they could not be generated or destroyed by any disturbance communicated to the shell, if the fluid be free from viscosity.

We proceed now to examine more closely the modes which depend on terms of the second order. As we have seen above, terms of different orders correspond to different fundamental modes; and therefore we may for the future suppose that the second order terms alone exist in $\psi_1$.

§ 5. Lamé Functions of Second Order.

A Lamé function of order $n$ is a function $R$ of one of the four forms

$$R = P_n, \quad R = \sqrt{\rho^3 - b^2}, \quad R = \sqrt{\rho^3 - c^2}, \quad R = \sqrt{(\rho^3 - b^2)(\rho^3 - c^2)}.$$

where $P_n$ denotes a rational, integral, algebraic function of $\rho$ of degree $n$, and $R$ satisfies the differential equation

$$(\rho^3 - b^2)(\rho^3 - c^2) \frac{d^2R}{d\rho^2} + \rho (2\rho^3 - b^2 - c^2) \frac{dR}{d\rho} = \left[ n(n + 1) \rho^3 - B \right] R \quad (20),$$

where $B$ is a suitably chosen constant.

The Lamé functions of the second order are, therefore, the three functions

$$\rho \sqrt{\rho^3 - b^2}, \quad \rho \sqrt{\rho^3 - c^2}, \quad \sqrt{(\rho^3 - b^2)(\rho^3 - c^2)},$$

together with two functions of the form $\rho^3 + \beta$. . . . . . . . . . . (21).

To find these latter functions, substitute in equation (20) with $n = 2$; we obtain

$$2(\rho^3 - b^2)(\rho^3 - c^2) + 2\rho^3 (2\rho^3 - b^2 - c^2) \equiv (6\rho^3 - B) (\rho^3 + \beta).$$

Equating coefficients of $\rho^3$, and the terms independent of $\rho$, we get

$$-4 (b^2 + c^2) = 6\beta - B, \quad 2b^2c^2 = -\beta B.$$
Eliminating $B$, the values of $\beta$ are given by

$$3\beta^2 + 2(\rho^2 + c^2)\beta + \rho^2 c^2 = 0 \ldots \ldots \ldots (23).$$

Let us now apply the formulae (16), (18), to the different forms of $R'$; take first

$$R' = \rho'(\rho^2 - b^2).$$

At the surface

$$M'N' = \mu' \sqrt{(\mu^2 - b^2)} \cdot \nu' \sqrt{(\nu^2 - \nu'^2)} = \frac{b\nu' \sqrt{(\nu^2 - \nu'^2)}}{\rho \sqrt{(\rho^2 - b^2)}} \ xy = b\nu' \sqrt{(\nu^2 - \nu'^2)} \ XY.$$

Therefore, when $\psi_1 = R'M'N'$,

$$\left\{ \begin{array}{l}
\frac{\partial \psi_1}{\partial x} \cos \alpha' + \frac{\partial \psi_1}{\partial y} \cos \beta' + \frac{\partial \psi_1}{\partial z} \cos \gamma' = P' \cdot \frac{2\rho^2 - b^2}{\rho \sqrt{(\rho^2 - b^2)}} \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ XY,
\frac{\partial \psi_1}{\partial y} \cos \alpha' - \frac{\partial \psi_1}{\partial x} \cos \beta' = P' \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ (X^2 - Y^2)
\end{array} \right\}$$

from (16)

$$\left\{ \begin{array}{l}
\frac{\partial \psi_1}{\partial y} \cos \alpha' - \frac{\partial \psi_1}{\partial x} \cos \beta' = P' \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ (X^2 - Y^2)
\end{array} \right\}$$

from (18)

Similarly, when $R' = \rho'(\rho^2 - c^2)$,

$$M'N' = \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ XZ \ at \ the \ surface,$$

and

$$\left\{ \begin{array}{l}
\frac{\partial \psi_1}{\partial x} \cos \alpha' + \frac{\partial \psi_1}{\partial y} \cos \beta' + \frac{\partial \psi_1}{\partial z} \cos \gamma' = P' \frac{2\rho^2 - c^2}{\rho \sqrt{(\rho^2 - c^2)}} \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ XZ,
\frac{\partial \psi_1}{\partial y} \cos \alpha' - \frac{\partial \psi_1}{\partial x} \cos \beta' = P' \sqrt{\frac{\rho^2 - c^2}{\rho^2 - b^2}} (-YZ)
\end{array} \right\}$$

and when $R' = \sqrt{(\rho^2 - b^2)}(\rho^2 - c^2)$,

$$M'N' = \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ YZ,$$

and

$$\left\{ \begin{array}{l}
\frac{\partial \psi_1}{\partial x} \cos \alpha' + \frac{\partial \psi_1}{\partial y} \cos \beta' + \frac{\partial \psi_1}{\partial z} \cos \gamma' = P' \frac{2\rho^2 - b^2 - c^2}{\sqrt{(\rho^2 - b^2)(\rho^2 - c^2)}} \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ XZ,
\frac{\partial \psi_1}{\partial y} \cos \alpha' - \frac{\partial \psi_1}{\partial x} \cos \beta' = P' \frac{\sqrt{(\rho^2 - c^2)}}{\rho} \ b\nu' \sqrt{(\nu^2 - \nu'^2)} \ YZ
\end{array} \right\}$$

(25); (26).

Take, now, the form (22). When

$$R = (\rho^2 + \beta), \ RMN = (\rho^2 + \beta)(\mu^2 + \beta)(\nu^2 + \beta);$$
but $p^3, \mu^2, v^2$ are the three roots of the equation in $\alpha$

$$\frac{x^2}{\alpha} + \frac{y^2}{\alpha - b^2} + \frac{z^2}{\alpha - c^2} = 1,$$

therefore,

$$(\alpha - p^3)(\alpha - \mu^2)(\alpha - v^2) \equiv \alpha(\alpha - b^2)(\alpha - c^2) - x^2(\alpha - b^2)(\alpha - c^2) - y^2\alpha(\alpha - c^2) - z^2\alpha(\alpha - b^2);$$

putting $\alpha = -\beta$ in this identity, we obtain

$$RMN = (\beta + p^3)(\beta + \mu^2)(\beta + v^2) = \beta(\beta + b^2)(\beta + c^2) + x^2(\beta + b^2)(\beta + c^2) + y^2\beta(\beta + c^2) + z^2\beta(\beta + b^2),$$

and, therefore, at the surface

$$RMN = (X^2 + Y^2 + Z^2)\beta(\beta + b^2)(\beta + c^2) + \rho^3X^3, (\beta + b^2)(\beta + c^2) + \rho^3 - b^2)Y^3, \beta(\beta + b^2) + (\rho^3 - c^2)Z^2, \beta(\beta + b^2)$$

or, since by (23) $(\beta + b^2)(\beta + c^2) = -\beta(\beta + c^2) - \beta(\beta + b^2)$,

$$RMN = (\rho^3 + \beta)[(\beta + b^2)(\beta + c^2)X^2 + \beta(\beta + c^2)Y^2 + \beta(\beta + b^2)Z^2],$$

therefore, when $R' = \rho^3 + \beta'$,

$$M'N' = \beta'(\beta' + c^2)(Y^2 - X^2) + \beta'(\beta' + b^2)(Z^2 - X^2),$$

and if $\psi_{1} = R'M'N'$$$
\frac{\partial \psi_{1}}{\partial x} \cos \alpha' + \frac{\partial \psi_{1}}{\partial y} \cos \beta' + \frac{\partial \psi_{1}}{\partial z} \cos \gamma'
= 2P' [\beta'(\beta' + c^2)(Y^2 - X^2) + \beta'(\beta' + b^2)(Z^2 - X^2)] . \quad (27),$$

and

$$\frac{\partial \psi_{1}}{\partial y} \cos \alpha' - \frac{\partial \psi_{1}}{\partial x} \cos \beta' = P' \frac{\rho^3 + \beta'}{\rho \sqrt{(\rho^3 - b^2)^2}} 2XY \{2\beta'(\beta' + c^2) + \beta'(\beta' + b^2)\},$$

or since $\beta'$ satisfies an equation similar to (23),

$$\frac{\partial \psi_{1}}{\partial y} \cos \alpha' - \frac{\partial \psi_{1}}{\partial x} \cos \beta' = -P' \frac{\rho^3 + \beta'}{\rho \sqrt{(\rho^3 - b^2)^2}} 2XY \{((c^2 + \beta')b^2)\}. \quad (28).$$

Let us denote by $\beta'_1, \beta'_2$, the two values of $\beta'$, and assume that MDCCXCXV. — A.
\[ \psi_1 = \lambda_1 (\rho^2 + \beta_1^2)(\mu^2 + \beta_1^2)(\nu^2 + \beta_1^2) + \lambda_2 (\rho^2 + \beta_2^2)(\mu^2 + \beta_2^2)(\nu^2 + \beta_2^2) \]
\[ + \frac{R_1}{\sqrt{(\beta_1^2 - \rho^2)} \sqrt{\beta_1^2 - \rho^2}} \rho \sqrt{(\beta_1^2 - \rho^2)}. \mu \sqrt{(\beta_1^2 - \rho^2)} \cdot \nu \sqrt{(\beta_1^2 - \rho^2)} \]
\[ + \frac{R_2}{\sqrt{(\beta_2^2 - \rho^2)} \sqrt{\beta_2^2 - \rho^2}} \rho \sqrt{(\beta_2^2 - \rho^2)}. \mu \sqrt{(\beta_2^2 - \rho^2)} \cdot \nu \sqrt{(\beta_2^2 - \rho^2)} \]
\[ + \frac{R_3}{\sqrt{(\beta_1^2 - \rho^2)} \sqrt{\beta_2^2 - \rho^2}} \sqrt{(\beta_1^2 - \rho^2)} \sqrt{(\beta_2^2 - \rho^2)}. \mu \sqrt{(\beta_2^2 - \rho^2)} \cdot \nu \sqrt{(\beta_2^2 - \rho^2)} \]

From equations (24) . . . (28), we see that (19) now takes the form

\[ \lambda_1 \left[ 2A_1 \{ \beta_1^2 (\beta_1^2 + \nu^2)(Y^2 - X^2) + \beta_1^2 (\beta_1^2 + \nu^2)(Z^2 - X^2) \} \right] \]
\[ + 2A_2 \{ \beta_2^2 (\beta_2^2 + \nu^2)(Y^2 - X^2) + \beta_2^2 (\beta_2^2 + \nu^2)(Z^2 - X^2) \} \]
\[ + B_1 \frac{2\rho^2 - \beta^2}{\rho \sqrt{\rho^2 - \beta^2}} XY + B_2 \frac{2\rho^2 - \beta^2}{\rho \sqrt{\rho^2 - \beta^2}} XZ + B_3 \frac{2\rho^2 - \beta^2 - \nu^2}{\sqrt{(\rho^2 - \beta^2)(\rho^2 - \nu^2)}} YZ \]
\[ - \frac{2 \omega i}{\rho \sqrt{\rho^2 - \beta^2}} \left[ - 2A_1 \beta_1^2 (\beta_1^2 + \nu^2)(\rho^2 + \beta_1^2)XY - 2A_2 \beta_2^2 (\beta_2^2 + \nu^2)(\rho^2 + \beta_2^2)XY \right] \]
\[ + B_1 \rho \sqrt{\rho^2 - \beta^2} (X^2 - Y^2) - B_2 \rho \sqrt{\rho^2 - \beta^2} YZ \]
\[ + B_3 \sqrt{(\rho^2 - \beta^2)(\rho^2 - \nu^2)} XZ \]
\[ = \lambda_1^2 \tau_1 \left[ \theta_1^2 \frac{\beta_1^2 - \beta^2}{\sqrt{(\rho^2 - \beta^2)(\rho^2 - \beta^2)}} YZ + \theta_2^2 \frac{\beta_2^2 - \beta^2}{\rho \sqrt{\rho^2 - \beta^2}} XZ + \theta_3^2 \frac{\beta_2^2 - \beta^2}{\rho \sqrt{\rho^2 - \beta^2}} YZ \right] \]

\[ \text{§ 6. Calculation of Coefficients in } \psi_1. \]

Equating coefficients of \( Y^2 - X^2, Z^2 - X^2 \) in the two members of (29)

\[ A_1 \beta_1^2 (\beta_1^2 + \nu^2) + A_2 \beta_2^2 (\beta_2^2 + \nu^2) + \frac{\omega i}{\lambda} B_1 = 0 \]
\[ A_1 \beta_1^2 (\beta_1^2 + \beta^2) + A_2 \beta_2^2 (\beta_2^2 + \beta^2) = 0 \]

Multiply the first of these by 2 and add to the second. Reducing by means of (23) we obtain

\[ b^5 \left[ - A_1 (\beta_1^2 + \beta^2) - A_2 (\beta_2^2 + \beta^2) \right] + \frac{2 \omega i}{\lambda} B_1 = 0 \]

Multiply by \( \frac{b^5}{b^3} \) and subtract from the first of equations (30); then

\[ A (\beta_1^2 + \beta^2) (\beta_1^2 + \beta^2) + A_2 (\beta_2^2 + \beta_2^2) (\beta_1^2 + \beta_2^2) + \frac{\omega i}{\lambda} \left( 1 - \frac{2 b^5}{b^5} \right) B_1 = 0. \]
But if we equate coefficients of $XY$ in (29) we obtain

$$B_1 (2\rho^2 - b^2) + \frac{4)i}{\lambda} b = [A_1 (\rho^2 + \beta'_1) (c^2 + \beta'_1) + A_2 (\rho^2 + \beta'_2) (c^2 + \beta'_2)] = - \lambda^2 \tau b^2 \theta'_3.$$

Hence

$$B_1 (2\rho^2 - b^2) + \frac{4}{\lambda^2} B_1 (b^2 - 2\rho^2) = - \lambda^2 \tau b^2 \theta'_3,$$

or

$$B_1 (2\rho^2 - b^2) \tau = - \lambda^2 \tau b^2 \theta'_3,$$

or

$$B_1 = - \frac{\lambda^2 b^2}{2 \rho^2 - b^2} \theta'_3 \ldots \ldots \ldots \ldots \ldots \ldots (32).$$

Again, equating coefficients of $XZ, YZ$ in (29), we have

$$B_2 \frac{2\rho^2 - c^2}{\rho \sqrt{(\rho^2 - c^2)}} - 2 \frac{\omega i}{\lambda} B_3 \sqrt{(\rho^2 - c^2)} = \frac{\lambda^2 \tau \theta'_2}{\rho \sqrt{(\rho^2 - c^2)}},$$

$$B_3 \frac{2\rho^2 - b^2 - c^2}{\sqrt{(\rho^2 - b^2)} (\rho^2 - c^2)} - 2 \frac{\omega i}{\lambda} B_2 \sqrt{(\rho^2 - b^2)} = - \lambda^2 \tau \theta'_1 \frac{c^2 - b^2}{\sqrt{(\rho^2 - b^2)} (\rho^2 - c^2)},$$

or, since $\rho^2 - c^2 = \tau^2 (\rho^2 - c^2)$

$$\begin{align*}
B_2 (2\rho^2 - c^2) - \frac{2\omega i}{\lambda} B_3 (\rho^2 - c^2) &= \lambda^2 \tau \theta'_2 \rho^2 \\
B_3 (2\rho^2 - b^2 - c^2) + \frac{2\omega i}{\lambda} B_2 (\rho^2 - c^2) &= - \lambda^2 \tau \theta'_1 (c^2 - b^2) \\
\end{align*} \ldots \ldots \ldots \ldots \ldots \ldots (33).$$

Now, as we have seen above,

$$\begin{align*}
A_1 (\rho^2 + \beta'_1) (\mu^2 + \beta'_1) (\nu^2 + \beta'_1) + A_2 (\rho^2 + \beta'_2) (\mu^2 + \beta'_2) (\nu^2 + \beta'_2) \\
&= A_1 \{\beta'_1 (\beta'_1 + b^2) (\beta'_1 + c^2) + \alpha^2 (\beta'_1 + b^2) (\beta'_1 + c^2) + y^2 \beta'_1 (\beta'_1 + c^2) + z^2 \beta'_1 (\beta'_1 + b^2)\} \\
&+ A_2 \{\beta'_2 (\beta'_2 + b^2) (\beta'_2 + c^2) + \alpha^2 (\beta'_2 + b^2) (\beta'_2 + c^2) + y^2 \beta'_2 (\beta'_2 + c^2) + z^2 \beta'_2 (\beta'_2 + b^2)\}
\end{align*}$$

which by (30) is equal to

$$\begin{align*}
A_1 \beta'_1 (\beta'_1 + b^2) + A_2 \beta'_2 (\beta'_2 + b^2) + \alpha^2 c^2 \{A_1 (\beta'_1 + b^2) + A_2 (\beta'_2 + b^2)\} + y^2 \left\{- \frac{\omega i}{\lambda} B_1 \right\} \\
= A_1 (\beta'_1 + b^2) \{ - \frac{2}{3} (b^2 + c^2) \beta'_1 - \frac{1}{3} b^2 c^2\} + A_2 (\beta'_2 + b^2) \{ - \frac{2}{3} (b^2 + c^2) \beta'_2 - \frac{1}{3} b^2 c^2\} \\
+ \frac{\omega i}{\lambda} B_1 (x^2 - y^2),
\end{align*}$$

3.2
and this by means of (30) and (31) reduces to
\[
\left\{ -\frac{1}{3}b^2 + (x^2 - y^2) \right\} \frac{\omega_1}{\lambda} B_1.
\]

Hence the complete value of \( \psi_1 \) is
\[
\frac{\omega_1}{\lambda} B_1 \left\{ -\frac{1}{3}b^2 + x^2 - y^2 \right\} + B_1 xy + B_2xz' + B_3yz' \\
= \frac{\omega_1}{\lambda} B_1 \left\{ -\frac{1}{3}b^2 + x^2 - y^2 \right\} + B_1 xy + \frac{B_2}{\tau} xz + \frac{B_3}{\tau} yz \ldots \ldots (34)
\]

where \( B_1, B_2, B_3 \) are given in terms of \( \theta', \theta'', \theta''' \) by equations (32), (33).

From equations (6), (34) it will be seen that, in the motions with which we are dealing, \( u, v, w \) are linear functions of \( x, y, z \). Hence the components of molecular rotation of the fluid, which involve first differential coefficients of \( u, v, w \), will be independent of \( x, y, z \). This justifies the assumption made in § 1 of the paper.

§ 7. Calculation of Couples on the Shell due to Fluid Pressure.

At any point of the fluid the pressure is given by (1); we have, viz.:
\[
p = \rho_1 \left\{ V_1 + \frac{1}{2} \omega^2 (x^2 + y^2) \right\} - \rho_1 \psi.
\]

Let us now refer to a new set of rectangular axes, \( Ox_1, Oy_1, Oz_1 \), coincident with the principal axes of the ellipsoid in its displaced position. The direction-cosines of one set of axes relatively to the other are given by the scheme

<table>
<thead>
<tr>
<th></th>
<th>( x_1 )</th>
<th>( y_1 )</th>
<th>( z_1 )</th>
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</thead>
<tbody>
<tr>
<td>( x )</td>
<td>1</td>
<td>(-\theta_3)</td>
<td>( \theta_2 )</td>
</tr>
<tr>
<td>( y )</td>
<td>( \theta_3 )</td>
<td>1</td>
<td>(-\theta_1)</td>
</tr>
<tr>
<td>( z )</td>
<td>(-\theta_2)</td>
<td>( \theta_1 )</td>
<td>1</td>
</tr>
</tbody>
</table>

Hence
\[
x = x_1 - y_1 \theta_3 + z_1 \theta_2, \\
y = y_1 - z_1 \theta_1 + x_1 \theta_3, \\
z = z_1 - x_1 \theta_2 + y_1 \theta_1,
\]
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and, neglecting squares of \( \theta_1, \theta_2, \theta_3 \), we obtain

\[
p = \rho_1 [V_1 + \frac{1}{2} \omega^2 (x_1^2 + y_1^2) - \omega^2 y_1 z_1 \theta_1 + \omega^3 x_1 z_1 \theta_2] - \rho_1 \psi \quad . . . (36),
\]

where in the small term \( \psi \) we may replace \( x, y, z \) by \( x_1, y_1, z_1 \).

If \( L, M, N \) denote the couples on the shell about the axes \( Ox_1, Oy_1, Oz_1 \)

\[
L = \int \int p \, d\sigma \left( \frac{P_{y_1 z_1}}{\rho^2 - c^2} - \frac{P_{y_1 z_1}}{\rho^2 - b^2} \right) = \frac{c^2 - b^2}{\rho^3 (\rho^3 - c^2)} \int \int P_{y_1 z_1} \, d\sigma,
\]

\[
M = \int \int p \, d\sigma \left( \frac{P_{x_1 y_1}}{\rho^2 - c^2} - \frac{P_{x_1 y_1}}{\rho^2 - b^2} \right) = \frac{-c^2}{\rho^3 (\rho^3 - c^2)} \int \int P_{x_1 y_1} \, d\sigma,
\]

\[
N = \int \int p \, d\sigma \left( \frac{P_{x_1 y_1}}{\rho^2 - b^2} - \frac{P_{x_1 y_1}}{\rho^2 - c^2} \right) = \frac{b^2}{\rho^3 (\rho^3 - b^2)} \int \int P_{x_1 y_1} \, d\sigma,
\]

where \( d\sigma \) is an element of the surface of the displaced ellipsoid, and the integrals are
taken over the whole surface.

Let us now consider separately the parts of these couples introduced by the
different terms in the expression (36) for \( p \).

(a) Take \( p = \rho_1 V_1 \).

The pressure at every point is the same as if the fluid were at rest under a
potential \( V_1 \).

\( V_1 \) will, in general, consist of three parts due respectively to (a) the attraction of the
shell; (\( \beta \)) the mutual attraction of the fluid particles; (\( \gamma \)) any external attracting
system.

If the part (a) gave rise to any couple, it would be exactly counterbalanced by the
couple on the shell due to the attraction of the fluid, since the attractions of the shell
on the fluid and of the fluid on the shell are equal and opposite.

The system of forces (\( \beta \)) also form a system in equilibrium, and, therefore, can
give rise to no resultant couple on the shell. Thus no couple can arise from the
mutual attractions of the parts of the system.

The pressure at any point due to the part (\( \gamma \)) is the same as if the fluid were at
rest. Thus the couples due to any external attracting system will be the same as if the
fluid were supposed to be solidified. If we add to these couples, due to the
attraction of the external system on the fluid, the parts due to the direct attraction
on the shell, we see that the total couples due to any external system will be the
same as if our system were solid throughout.

(b.) Take

\[
p = \frac{1}{2} \omega^2 \rho_1 (x_1^2 + y_1^2) - \omega^3 \rho_1 z_1 (y_1 \theta_1 - x_1 \theta_2) \quad .
\]

Integrating over the surface of the ellipsoid

\[
\frac{x_1^2}{\rho^2} + \frac{y_1^2}{\rho^2 - b^2} + \frac{z_1^2}{\rho^2 - c^2} = 1,
\]
we have

\[
\int\! P \, d\sigma \, x_1^2 \, y_1 = 0, \quad \int\! P \, d\sigma \, y_1^2 \, z_1 = 0,
\]

\[
\int\! P \, d\sigma \, y_1^2 \, z_1 = \frac{4}{3} \pi \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2), \quad \&c.
\]

Therefore,

\[
\int\! P \, d\sigma \, y_1 z_1 = - \omega^2 \theta_1 \rho_1 \cdot \frac{4}{3} \pi \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2),
\]

and the corresponding part of \( L \) is

\[- \frac{4}{3} \pi \rho_1 \cdot \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} \omega^2 \theta_1.\]

Similarly the parts of \( M, N \) arising from this part of \( P \) are

\[+ \frac{4}{3} \pi \rho_1 \cdot \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} (c^2 - b^2) \omega^2 \theta_2 \text{ and } 0.\]

(c.) Lastly, if

\[p = - \rho_1 \psi = - \rho_1 e^{\lambda \tau} \left[ \frac{\omega}{\lambda} B_1 \left\{ x_1^2 - y_1^2 - \frac{1}{2} b^2 \right\} + B_1 x_1 y_1 + \frac{B_2}{\tau} x_1 z_1 + \frac{B_2}{\tau} y_1 z_1 \right],\]

\[\frac{e^2 - b^2}{\rho^2 - b^2} \int\! P \, d\sigma \, y_1 z_1 = - \frac{4}{3} \pi \rho_1 (e^2 - b^2) \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} \frac{B_2}{\tau} e^{\lambda \tau},\]

\[\frac{e^2 - b^2}{\rho^2 - b^2} \int\! P \, d\sigma \, y_1 x_1 = + \frac{4}{3} \pi \rho_1 e^2 \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} \frac{B_2}{\tau} e^{\lambda \tau},\]

\[\frac{e^2 - b^2}{\rho^2 - b^2} \int\! P \, d\sigma \, y_1 x_1 = - \frac{4}{3} \pi \rho_1 b^2 \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} B_1 e^{\lambda \tau}.\]

Collecting the different parts, we obtain for the couples, provided there be no external disturbing force,

\[L = - \frac{4}{3} \pi \rho_1 \cdot \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} (e^2 - b^2) \left\{ \omega^2 \theta_1 + \frac{B_2}{\tau} e^{\lambda \tau} \right\},\]

\[M = + \frac{4}{3} \pi \rho_1 \cdot \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} e^2 \left\{ \frac{B_2}{\tau} e^{\lambda \tau} - \omega^2 \theta_2 \right\},\]

\[N = - \frac{4}{3} \pi \rho_1 \cdot \rho (\rho^2 - b^2)^{1} (\rho^2 - c^2)^{1} b^2 \cdot B_1 e^{\lambda \tau} = (\mu - \nu) B_1 e^{\lambda \tau}.\]
where, for brevity, we have put

\[ \nu = \frac{1}{3} \pi \rho_1 \cdot \rho (c^2 - b^2)^3 (c^2 - b^2), \quad \mu = \frac{1}{3} \pi \rho_1 \cdot \rho (c^2 - b^2)^3 (c^2 - b^2) . \] (38).

The terms in \( \omega^2 \) arising from (b) are due to the centrifugal force of the fluid, and occur in consequence of the axis of rotation of the shell not accurately coinciding with that of the fluid, while the terms (c) are due to the effective inertia of the fluid.

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values given in (37). If there be any external attracting system we must add to the right-hand members the couples due to this system, estimated as though the system were rigid throughout. In dealing with the "free" oscillations, however, we may omit these terms.

Introducing the values of \( p, q, r \) from (39) and omitting small quantities of the second order

\[
\begin{align*}
A\dot{\theta}_1 - (B - C) \omega^2 \theta_1 - \omega \dot{\theta}_2 (A + B - C) &= L, \\
B\dot{\theta}_2 + (C - A) \omega^2 \theta_2 + \omega \dot{\theta}_1 (A + B - C) &= M, \\
C\dot{\theta}_3 &= N.
\end{align*}
\]

Hence, on replacing \( L, M, N \) by their values (37), putting \( \theta_1 = \theta_1 e^{\omega t}, \) &c., and omitting the time factor, we obtain

\[
\begin{align*}
\theta_1 \left\{ A\lambda^2 + (B - C) \omega^2 \right\} + i\lambda \omega \theta_2 (A + B - C) - \nu \left\{ \omega^2 \theta_1 + \frac{B_3}{\tau} \right\} &= 0 \\
\theta_2 \left\{ B\lambda^2 + (A - C) \omega^2 \right\} - i\lambda \omega \theta_1 (A + B - C) - \mu \left\{ \omega^2 \theta_2 - \frac{B_3}{\tau} \right\} &= 0
\end{align*}
\]

\[
\theta_3 \left\{ C\lambda^2 \right\} - (\mu - \nu) B_1 = 0
\]

from (32)

\[
B_1 = -\frac{\lambda^2 \xi^2}{(2\rho^2 - b^2) \theta_3}.
\]

Hence the freedom defined by the coordinate \( \theta_3 \) is neutral, and a disturbance, which causes the coordinate \( \theta_3 \) to vary, will not give rise to an oscillatory motion.

From (33) the values of \( B_2/\tau, B_3/\tau \) are given by

\[
\begin{align*}
\frac{B_3}{\tau} (2\rho^2 - c^2) - \frac{2\omega i}{\lambda} \frac{B_3}{\tau} (\rho^2 - c^2) - \lambda^2 \xi^2 \theta_3 &= 0 \\
\frac{B_3}{\tau} (2\rho^2 - b^2 - c^2) + \frac{2\omega i}{\lambda} \frac{B_2}{\tau} (\rho^2 - c^2) + \lambda^2 (c^2 - b^2) \theta_1 &= 0
\end{align*}
\]

Eliminating \( \theta_1', \theta_2', B_2/\tau, B_3/\tau \) from (40), (41) by means of a determinant, the periods of free oscillation are given by

\[
\begin{vmatrix}
A\lambda^2 + (B - C - \nu) \omega^2, & i\lambda \omega (A + B - C), & 0, & \nu \\
-i\lambda \omega (A + B - C), & B\lambda^2 + (A - C - \mu) \omega^2, & \mu, & 0 \\
0, & -\lambda^2 \xi^2, & 2\rho^2 - c^2, & -\frac{2\omega i}{\lambda} (\rho^2 - c^2) \\
\lambda^2 (c^2 - b^2), & 0, & \frac{2\omega i}{\lambda} (\rho^2 - c^2), & 2\rho^2 - b^2 - c^2
\end{vmatrix} = 0.
\]

Expanding out this determinant, we obtain

\[
\begin{align*}
\{ [\lambda \lambda^2 - (C - B + \nu) \omega^2] \} & \{ [\lambda \lambda^2 - (C - A + \mu) \omega^2] \} - \omega^2 \lambda^2 (A + B - C) \omega \\
& \times \left[ (2\rho^2 - c^2) (2\rho^2 - b^2 - c^2) - \frac{4\omega^2}{\lambda^3} (\rho^2 - c^2)^2 \right] \\
& \mu \omega^2 \lambda^2 \lambda^2 [\lambda \lambda^2 - (C - B + \nu) \omega^2] (2\rho^2 - b^2 - c^2) \\
& + \nu (c^2 - b^2) [\lambda \lambda^2 - (C - A + \mu) \omega^2] (2\rho^2 - c^2) \\
& - 2\omega^2 \lambda^2 (\rho^2 - c^2) (A + B - C) [\mu (c^2 - b^2) + \nu c^2] \\
& + \mu \nu \lambda^2 \lambda^2 (\omega^2 - c^2) (c^2 - b^2) = 0 \\
\end{align*}
\]

Now since

\[
\rho^2 - c^2 = \tau^2 (\rho^2 - c^2) = \left( 1 - \frac{4\omega^2}{\lambda^2} \right) (\rho^2 - c^2),
\]

\[
(2\rho^2 - c^2) (2\rho^2 - b^2 - c^2) - \frac{4\omega^2}{\lambda^3} (\rho^2 - c^2)^2
\]

\[
= \rho^2 (\rho^2 - b^2) + (\rho^2 + \rho^2 - b^2) (\rho^2 - c^2) + (\rho^2 - c^2)^2 \left( 1 - \frac{4\omega^2}{\lambda^2} \right)
\]

\[
= \frac{1}{\tau^2} \cdot \{ \tau^2 \rho^2 (\rho^2 - b^2) + (2\rho^2 - b^2) (\rho^2 - c^2) + (\rho^2 - c^2)^2 \}
\]

\[
= \frac{1}{\lambda^2 \tau^2} \cdot \{ \lambda^2 (2\rho^2 - c^2) (2\rho^2 - b^2 - c^2) - 4\omega^2 \rho^2 (\rho^2 - b^2) \}
\]

\[
2\rho^2 - b^2 - c^2 = \frac{1}{\tau^2} \cdot \{ \tau^2 (\rho^2 - b^2) + (\rho^2 - c^2) \}
\]

\[
= \frac{1}{\lambda^2 \tau^2} \cdot \{ \lambda^2 (2\rho^2 - b^2 - c^2) - 4\omega^2 (\rho^2 - b^2) \}
\]

and

\[
2\rho^2 - c^2 = \frac{1}{\tau^2} \cdot \{ \tau^2 \rho^2 + (\rho^2 - c^2) \} = \frac{1}{\lambda^2 \tau^2} \cdot \{ \lambda^2 (2\rho^2 - c^2) - 4\omega^2 \rho^2 \}
\]

Hence substituting in (42) we obtain the following cubic for \( \lambda^2 \):

\[
\begin{align*}
\{ [\lambda \lambda^2 - (C - B + \nu) \omega^2] \} & \{ [\lambda \lambda^2 - (C - A + \mu) \omega^2] \} - \omega^2 \lambda^2 (A + B - C) \omega \\
& \times \left[ \lambda^2 (2\rho^2 - b^2 - c^2) (2\rho^2 - c^2) - 4\omega^2 \rho^2 (\rho^2 - b^2) \right] \\
& \mu \omega^2 \lambda^2 \lambda^2 [\lambda \lambda^2 - (C - B + \nu) \omega^2] (2\rho^2 - b^2 - c^2) \\
& + \nu (c^2 - b^2) \lambda^2 [\lambda \lambda^2 - (C - A + \mu) \omega^2] (2\rho^2 - c^2) \\
& - 2\omega^2 \lambda^4 (\rho^2 - c^2) (A + B - C) [\mu (c^2 - b^2) + \nu c^2] \\
& + \mu \nu \lambda^4 (\lambda^2 - 4\omega^2) \omega (c^2 - b^2) = 0.
\end{align*}
\]
Let us now change our notation, replacing \( \rho^2, \beta^2, \gamma^2 \) by \( \alpha^2, \beta^2, \gamma^2 \); the period equation may then be written

\[
\{ \alpha \lambda^2 + (B - C - \nu) \omega^2 \} \{ B \lambda^2 + (A - C - \mu) \omega^2 \} - \omega^2 \lambda^2 (A + B - C)^2 \times [ \lambda^2 (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) - 4 \omega^2 \alpha^2 \beta^2 ]
\]

\[
+ \mu (\alpha^2 - \gamma^2) \lambda^2 \{ \alpha \lambda^2 + (B - C - \nu) \omega^2 \} \{ B \lambda^2 + (A - C - \mu) \omega^2 \} \{ \lambda^2 (\beta^2 + \gamma^2) - 4 \omega^2 \beta^2 \}
\]

\[
+ \nu (\beta^2 - \gamma^2) \lambda^2 \{ B \lambda^2 + (A - C - \mu) \omega^2 \} \{ \lambda^2 (\alpha^2 + \gamma^2) - 4 \omega^2 \alpha^2 \}
\]

\[
- 2 \omega^2 \lambda^3 \gamma^2 (A + B - C) \{ \mu (\beta^2 - \gamma^2) + \nu (\alpha^2 - \gamma^2) \} - 3 \mu \nu \omega^3 (\alpha^2 - \gamma^2) (\beta^2 - \gamma^2)
\]

\[
\gamma^3 \lambda^2 (A + B - C) \{ \mu (\beta^2 - \gamma^2) + \nu (\alpha^2 - \gamma^2) \} - 3 \mu \nu \omega^3 (\alpha^2 - \gamma^2) (\beta^2 - \gamma^2)
\]

\[
= - \omega^3 (A + B - C) \left[ \mu \{ (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) - 4 \alpha^2 \beta^2 + (\gamma^2 - \alpha^2) (\gamma^2 - 3 \beta^2) - 2 \gamma^2 (\gamma^2 - \beta^2) \} \right]
\]

\[
+ \nu \{ (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) - 4 \alpha^2 \beta^2 + (\gamma^2 - \alpha^2) (\gamma^2 - 3 \beta^2) - 2 \gamma^2 (\gamma^2 - \beta^2) \}
\]

\[
+ \mu \nu \omega^3 \left( (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) - 4 \alpha^2 \beta^2 + (\gamma^2 - \alpha^2) (\gamma^2 - 3 \beta^2) - 3 \gamma^2 (\gamma^2 - \beta^2) \right)
\]

therefore \( \lambda^2 = \omega^2 \) is always one root of (44).

Arranging (44) according to powers of \( \lambda^2 \), we have

\[
\lambda^0 \left[ - A B (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) + \mu A (\beta^2 + \gamma^2) (\alpha^2 - \gamma^2) + \nu B (\alpha^2 + \gamma^2) (\beta^2 - \gamma^2) \right]
\]

\[
+ \mu \nu (\alpha^2 - \gamma^2) (\beta^2 - \gamma^2)
\]

\[
- \omega^2 \lambda^4 \left[ (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) \{ (A + B - C)^2 - A(A - C - \mu) - B(B - C - \nu) \} + 4 A B \alpha^2 \beta^2 \right]
\]

\[
- \mu (\alpha^2 - \gamma^2) \{ (\beta^2 + \gamma^2) (B - C - \nu) - 4 A \beta^2 \}
\]

\[
- \nu (\beta^2 - \gamma^2) \{ (\alpha^2 + \gamma^2) (A - C - \mu) - 4 B \alpha^2 \}
\]

\[
+ 2 \gamma^2 (A + B - C) \{ \mu (\beta^2 - \gamma^2) + \nu (\alpha^2 - \gamma^2) \}
\]

\[
+ 4 \mu \nu (\alpha^2 - \gamma^2) (\beta^2 - \gamma^2)
\]

\[
+ \omega^3 \lambda^2 \left[ (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) (B - C - \nu) (A - C - \mu) \right]
\]

\[
+ 4 \alpha \beta^2 \{ (A + B - C)^2 - A(A - C - \mu) - B(B - C - \nu) \}
\]

\[
- 4 \mu \beta^2 (\alpha^2 - \gamma^2) (B - C - \nu) - 4 \nu \alpha^2 (\beta^2 - \gamma^2) (A - C - \mu)
\]

\[
- \omega^6 \left[ 4 \alpha \beta^2 (B - C - \nu) (A - C - \mu) \right] = 0.
\]

Dividing out by the factor \( \lambda^2 - \omega^2 \), we are left with
\[ \lambda^4 \left[ A (\beta^2 + \gamma^2) + \nu (\beta^2 - \gamma^2) \right] \\
- \omega^2 \lambda^2 \left[ (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) (B - C - \nu) (A - C - \mu) + 4 \alpha^2 \beta^2 (A - C - \mu) \right] \\
+ 4 \mu \beta^2 \left( (\alpha^2 - \gamma^2) (B - C - \nu) + 4 \nu \alpha^2 (\beta^2 - \gamma^2) (A - C - \mu) \right) \\
+ \omega^4 \cdot \{4 \alpha^2 \beta^2 (B - C - \nu) (A - C - \mu) \} = 0, \]

or

\[ \lambda^4 \left[ A (\beta^2 + \gamma^2) + \nu (\beta^2 - \gamma^2) \right] \\
- \omega^2 \lambda^2 \left[ (\alpha^2 + \gamma^2) (\beta^2 + \gamma^2) (B - C - \nu) (A - C - \mu) + 4 \alpha^2 \beta^2 (A + \nu) (B + \mu) \right] \\
+ 4 \mu \beta^2 \gamma^2 \cdot (B - C - \nu) + 4 \nu \alpha^2 \gamma^2 (A - C - \mu) \\
+ \omega^4 \cdot \{4 \alpha^2 \beta^2 (B - C - \nu) (A - C - \mu) \} = 0. \] (45)

In order that the system may satisfy the criteria for "ordinary" stability the roots of this equation in \( \lambda^2 \) must be real and positive.

The period equation (45) agrees with the equation (5) (§ 1), and the solution of it, in the case in which the ellipsoid differs but slightly from a sphere is given in § 3.


From equations (40), (41), (43) we see that the equations giving the ratios of the quantities \( \theta_1', \theta_2', B_2/\tau, B_3/\tau \) are

\[ \theta_1' \left\{ A \lambda^2 + (B - C) \omega^2 \right\} + i \lambda \omega \theta_2' (A + B - C) - \nu \left( \omega^2 \theta_1' + \frac{B_3}{\tau} \right) = 0, \]

\[ \theta_2' \left\{ B \lambda^2 + (A - C) \omega^2 \right\} - i \lambda \omega \theta_1' (A + B - C) - \mu \left( \omega^2 \theta_2' + \frac{B_3}{\tau} \right) = 0, \]

\[ \theta_1' \left\{ (\alpha^2 + \gamma^2) \lambda^2 - 4 \omega^2 \alpha^2 \right\} - 2 \omega i \lambda \gamma^2 \frac{B_3}{\tau} - \lambda^2 (\lambda^2 - 4 \omega^2) (\alpha^2 - \gamma^2) \theta_2' = 0, \]

\[ \theta_2' \left\{ (\beta^2 + \gamma^2) \lambda^2 - 4 \omega^2 \beta^2 \right\} + 2 \omega i \lambda \gamma^2 \frac{B_3}{\tau} + \lambda^2 (\lambda^2 - 4 \omega^2) (\beta^2 - \gamma^2) \theta_1' = 0. \] (46)

(a). We have seen that in every case \( \lambda^2 = \omega^2 \) is one root of the period equation; when \( \lambda = \omega \) the equations (46) reduce to

\[ \theta_1' \left\{ A + B - C - \nu \right\} + i \theta_2' (A + B - C) - \nu \frac{B_3}{\tau \omega^2} = 0, \]

\[ \theta_2' \left\{ A + B - C - \mu \right\} - i \theta_1' (A + B - C) + \mu \frac{B_3}{\tau \omega^2} = 0, \]

\[ \frac{B_3}{\tau \omega^2} (\gamma^2 - 3 \alpha^2) - 2 i \gamma^2 \frac{B_3}{\tau \omega^2} + 3 (\sigma^2 - \gamma^2) \theta_2' = 0, \]

\[ \frac{B_3}{\tau \omega^2} (\gamma^2 - 3 \beta^2) + 2 i \gamma^2 \frac{B_3}{\tau \omega^2} - 3 (\beta^2 - \gamma^2) \theta_1' = 0, \]

\[ 3 \sigma^2. \]
which are satisfied by
\[ \theta_1' = -i\theta_2' = - \frac{B_5}{\tau \omega^2} = -i \frac{B_2}{\tau \omega^2}. \]

Suppose \( \theta_1 = \phi e^{i(\omega t + \epsilon)} \) where \( \phi \) is a real quantity; we have as one solution
\[ \theta_1 = \phi e^{i(\omega t + \epsilon)}, \quad \theta_2 = i\phi e^{i(\omega t + \epsilon)}. \]

Changing the sign of \( i \) wherever it occurs, another solution is given by
\[ \theta_1 = \phi e^{-i(\omega t + \epsilon)}, \quad \theta_2 = -i\phi e^{-i(\omega t + \epsilon)} \]
and this corresponds to the value \(-\omega \) of \( \lambda \).

Combining these two solutions we get as the real motion corresponding to the root \( \lambda^2 = \omega^2 \),
\[ \theta_1 = 2\phi \cos(\omega t + \epsilon), \quad \theta_2 = -2\phi \sin(\omega t + \epsilon). \]

Now \( \theta_1, \theta_2 \) serve to determine the position of that principal axis which in the steady motion coincides with the axis of rotation, relatively to axes which are themselves revolving with angular velocity \( \omega \).

Let us consider the angular displacements relatively to fixed axes \( O\xi, O\eta, O\zeta \) coincident with the position occupied by the moving axes at the time \( t = 0 \); they are
\[ \theta_1 \cos \omega t - \theta_2 \sin \omega t = 2\phi \cos \epsilon, \]
\[ \theta_1 \sin \omega t + \theta_2 \cos \omega t = -2\phi \sin \epsilon, \]
and these are constant quantities. Thus, the apparent oscillation which corresponds to the root \( \lambda^2 = \omega^2 \), consists of a small permanent displacement of the axis of rotation, and the system rotates as if rigid about an axis which does not accurately coincide with our axis \( Oz \). It is obvious that if \( \omega \) be the angular velocity of rotation about this axis, the system and the moving axes \( Ox, Oy, Oz \) will return to their original positions after an interval \( 2\pi/\omega \), and, therefore, the system will appear to oscillate in a period \( 2\pi/\omega \) relatively to these moving axes.

It is easy to see that the fluid motion, indicated by the analysis, also consists of a motion of pure rotation.

For when \( \theta_1 = \phi e^{i(\omega t + \epsilon)} \)
\[ B_1 = 0 \quad B_2/\tau \omega^2 = -iB_3/\tau \omega^2 = i\phi e^{\epsilon}. \]

Therefore, from (34),
\[ \psi_1 = \omega^5 i\phi e^{\epsilon} \{xz + iyz\}, \]
and from (6),
ROTATING ELLIPSOIDAL SHELL CONTAINING FLUID.

\[ u_1 = \frac{1}{3\omega} \{ -\phi \omega z e^{it} - 2\phi \omega z e^{it} \} = -\phi \omega z e^{it} \]
\[ v_1 = \frac{1}{3\omega} \{ -i\phi \omega z e^{it} - 2i\phi \omega z e^{it} \} = -\phi z i e^{it} \]
\[ w_1 = \phi \omega (x + iy) e^{it}, \]

whence
\[ u = -\phi \omega z e^{i(\omega t + \epsilon)}, \quad v = -\phi z i e^{i(\omega t + \epsilon)}, \quad w = \phi \omega (x + iy) e^{i(\omega t + \epsilon)}, \]
and, in the corresponding real solution,
\[ u = -2\phi \omega \cos(\omega t + \epsilon), \quad v = 2\phi \omega \sin(\omega t + \epsilon), \]
\[ w = 2\phi \omega [x \cos(\omega t + \epsilon) - y \sin(\omega t + \epsilon)]. \]

These are the component velocities relatively to the moving axes. The velocities parallel to the instantaneous positions of the moving axes are
\[ u - y \omega, \quad v + x \omega, \quad w. \]

The velocities parallel to the fixed Oξ, η, ξ, are therefore
\[ (u - y \omega) \cos \omega t - (v + x \omega) \sin \omega t = -2\phi \omega \cos \epsilon - \omega \eta, \]
\[ (v + x \omega) \cos \omega t + (u - y \omega) \sin \omega t = 2\phi \omega \sin \epsilon + \omega \xi, \]
\[ w = 2\phi \omega \{\xi \cos \epsilon - \eta \sin \epsilon\}. \]

Thus the fluid motion is a motion of pure rotation, the component angular velocities about the axes being
\[ -2\phi \omega \sin \epsilon, \quad -2\phi \omega \cos \epsilon, \quad \omega. \]

The resultant of these angular velocities is an angular velocity \( \omega \) about the line whose direction cosines are
\[ -2\phi \sin \epsilon, \quad -2\phi \cos \epsilon, \quad 1. \]

The similar case for the spheroid with a free surface has been already discussed by Bryan ('Phil. Trans.,' 1889).

(b). Next take
\[ \lambda = \omega [1 + (\epsilon_1 + \epsilon_2) (1 + \eta)] = \omega (1 + E) \text{ say} \]
where
\[ E = \frac{1}{2} (\epsilon_1 + \epsilon_2) (1 + \eta). \]

Substituting this value of \( \lambda \) in (46) and putting \( \alpha = \gamma (1 + \epsilon_1), \&c. \), we obtain
\[
\theta'\{A + B - C + 2AE - qCe_3\} + i\theta'\{A + B - C\} (1 + E) - qCe_3 \frac{B_a}{\tau \omega^2} = 0, \\
B'\{A + B - C\} + 2BE - qCe_1 - \theta'\{A + B - C\} (1 + E) + qCe_1 \frac{B_b}{\tau \omega^2} = 0, \\
\frac{B_a}{\tau \omega^2} \{1 + \epsilon_1 - E\} + 1 + \epsilon_1 - E, (1 + E) = 0, \\
\frac{B_b}{\tau \omega^2} \{1 + \epsilon_2 - E\} - 1 + \epsilon_2 - E, (1 + E) = 0. \\
\]

These equations are correct as far as first powers of \(\epsilon_1, \epsilon_2, E\) only. Solving for the ratios of \(\theta_1', \theta_2', B_a/\tau \omega^2, B_b/\tau \omega^2\), we have

\[
\begin{pmatrix}
\theta_1' \\
\theta_2'
\end{pmatrix} = \begin{pmatrix}
\frac{A + B - C + 2BE - qCe_1}{1 + \epsilon_1 - E, (1 + E)} & \frac{qCe_1}{\epsilon_2 (3 + 2E)} \\
-3\epsilon_1 & -i(1 + E)
\end{pmatrix} \begin{pmatrix}
\frac{\epsilon_1}{1 + \epsilon_1 - E, (1 + E)} & \frac{qCe_1}{\epsilon_2 (3 + 2E)} \\
0 & -i(1 + E)
\end{pmatrix} + \begin{pmatrix}
\frac{B_a}{\tau \omega^2} \\
\frac{B_b}{\tau \omega^2}
\end{pmatrix}
\]

or

\[
\frac{\theta_1'}{\epsilon_1 + \epsilon_2 - 4E} = \frac{-i\theta_2'}{3(\epsilon_1 + \epsilon_2)(A + B - C) - \epsilon_1 + \epsilon_2 - 4E} = \frac{-iB_a}{\tau \omega^2} \left(\frac{\epsilon_1 + \epsilon_2}{3(A + B - C)}\right) = \frac{-B_b}{\tau \omega^2} \left(\frac{\epsilon_1 + \epsilon_2}{3(A + B - C)}\right),
\]

where the denominators are correct as far as first powers of \(\epsilon_1, \epsilon_2\), &c., only.

Replacing \(E\) by its value \(\frac{1}{2} (\epsilon_1 + \epsilon_2) (1 + q)\) we obtain

\[
\frac{\theta_1'}{2q + 1} = \frac{i\theta_2'}{2q + 1} = \frac{-iB_a}{3\tau \omega^2} = \frac{-B_b}{3\tau \omega^2}.
\]

Taking

\[
\theta_1' = \phi e^{i\epsilon}
\]

we have

\[
\theta_2' = i\phi e^{i\epsilon}
\]

and, in the corresponding real motion,

\[
\theta_1 = 2\phi \cos (\lambda t + \epsilon), \\
\theta_2 = -2\phi \sin (\lambda t + \epsilon).
\]

The angular displacements, relatively to the fixed axes \(O\xi, O\eta, O\zeta\), at time \(t\) are
\[ \begin{align*}
\theta_1 \cos \omega t - \theta_2 \sin \omega t &= 2\phi \cos \left[ (\lambda - \omega) t + \epsilon \right], \\
\theta_1 \sin \omega t + \theta_2 \cos \omega t &= -2\phi \sin \left[ (\lambda - \omega) t + \epsilon \right].
\end{align*} \]

Thus the motion of the principal axis consists approximately of a simple harmonic motion in period \(2\pi/(\lambda - \omega) = 2\pi/E\omega\), in virtue of which it describes a small cone about its mean position in a direction opposite to that in which the system is rotating.

The position of the instantaneous axis of rotation of the shell is defined by the direction cosines

\[ \dot{\theta}_1/\omega, \quad \dot{\theta}_1/\omega, \quad 1, \]

or

\[ -2\phi \frac{\lambda}{\omega} \sin (\lambda t + \epsilon), \quad -2\phi \frac{\lambda}{\omega} \cos (\lambda t + \epsilon), \quad 1; \]

and since \(\lambda\) is approximately equal to \(\omega\), this axis will be very nearly coincident with the principal axis. From (48) we have also

\[ \frac{B_2}{\tau \omega^2} = -i \frac{B_3}{\tau \omega^2} = -\frac{3}{1 + 2q} i\theta'_1 = -\frac{3}{1 + 2q} i\phi e^b, \]

and therefore from (34)

\[ \psi_1 = -\frac{3}{1 + 2q} i\phi \omega^2 (x + iy) e^b; \]

to the same order of approximation we have

\[ u_1 = \frac{3}{1 + 2q} \phi \omega x e^b, \quad v_1 = \frac{3}{1 + 2q} \phi \omega y e^b, \quad \omega_1 = -\frac{3}{1 + 2q} \phi \omega (x + iy) e^b. \]

Whence, in the corresponding real solution

\[ u = \frac{6}{1 + 2q} \phi \omega x \cos (\lambda t + \epsilon), \quad v = -\frac{6}{1 + 2q} \phi \omega x \sin (\lambda t + \epsilon), \quad w = \frac{6}{1 + 2q} \phi \omega \left[ -x \cos (\lambda t + \epsilon) + y \sin (\lambda t + \epsilon) \right]. \]

The velocity components relative to the fixed axes are therefore

\[ \begin{align*}
(u - y\omega) \cos \omega t - (v + x\omega) \sin \omega t &= \frac{6}{1 + 2q} \phi \omega x \cos (\lambda - \omega t + \epsilon) - \omega \eta, \\
(v + x\omega) \cos \omega t + (u - y\omega) \sin \omega t &= -\frac{6}{1 + 2q} \phi \omega x \sin (\lambda - \omega t + \epsilon) + \omega \xi, \\
w &= -\frac{6}{1 + 2q} \phi \omega \left\{ \xi \cos (\lambda - \omega t + \epsilon) - \eta \sin (\lambda - \omega t + \epsilon) \right\}. 
\end{align*} \]
Hence, the motion of the fluid will consist very approximately of a rotation, as if rigid, with angular velocity $\omega$ about the line whose direction-cosines are

$$\frac{6}{1 + 2q} \phi \sin (\lambda - \omega t + \epsilon), \quad \frac{6}{1 + 2q} \phi \cos (\lambda - \omega t + \epsilon),$$

This axis will itself describe a cone in period $2\pi/E\omega$, and it will be so situated that the axis $Oz$ lies in the plane containing the axes of revolution of the fluid and of the shell, and is between these two axes. The semi-vertical angles of the cones described by the axes of rotation of fluid and the shell will be in the ratio $3 : 2q + 1$.

The motion under discussion is that which would ensue if the shell were set rotating about its principal axis, while the fluid possessed a rotatory motion in the same period about some other axis. It is clear, that as $\epsilon_1$, $\epsilon_2$, and consequently $E$, diminish, the period of this oscillation will be prolonged; that is to say, the motion of the axes of rotation will become slower. This motion will be reduced to zero when $\epsilon_1$, $\epsilon_2$ vanish. In this case the internal surface of the shell is spherical, and the shell and fluid, of course, move independently. So far as this (apparent) oscillation is concerned, they will each be rotating with angular velocity $\omega$, but about different axes.

From the expression for the ratio of the amplitudes, we see that when $q$ is large, that is when the effective inertia of the fluid is large, compared with that of the shell, the disturbance of the shell will be considerable, compared with that of the fluid; whereas if $q$ be small, the disturbance of the shell bears to that of the fluid, a ratio which approximates to, but is always in excess of, $1 : 3$.

This oscillation has been previously examined by Hopkins (Phil. Trans., 1839) under certain special assumptions, as to the initial circumstances, and to the law of distribution of density in the shell.

(c). Lastly, suppose $\lambda = \omega \sqrt{(\kappa_1 + q\epsilon_1)} (\kappa_2 + q\epsilon_2)$.

The approximate form of equations (46) is now

$$\theta'_1 \{\kappa_2 + q\epsilon_2\} B - i \theta'_2 B \sqrt{(\kappa_1 + q\epsilon_1)}(\kappa_2 + q\epsilon_2) + q \epsilon_2 B_2 \frac{B_3}{\tau} = 0,$$

$$\theta'_2 \{\kappa_1 + q\epsilon_1\} A + i \theta'_1 A \sqrt{(\kappa_1 + q\epsilon_1)}(\kappa_2 + q\epsilon_2) - q \epsilon_1 B_1 \frac{B_3}{\tau} = 0,$$

$$2 \frac{B_3}{\tau} (1 + 2\epsilon_1) + i \sqrt{(\kappa_1 + q\epsilon_1)}(\kappa_2 + q\epsilon_2) B_2 \frac{B_3}{\tau} = 0,$$

$$2 \frac{B_3}{\tau} (1 + 2\epsilon_2) - i \sqrt{(\kappa_1 + q\epsilon_1)}(\kappa_2 + q\epsilon_2) B_2 \frac{B_3}{\tau} = 0.$$

Hence approximately $B_2/\tau = B_3/\tau = 0$, and

$$\frac{\theta'_1}{\sqrt{(\kappa_1 + q\epsilon_1)}} = \frac{i \theta'_2}{\sqrt{(\kappa_2 + q\epsilon_2)}} = \phi \omega^i, \text{ say}.$$
therefore
\[ \theta_1 = \phi \sqrt{(\kappa_1 + q\epsilon_1)} e^{i(\omega t + \epsilon)}, \]
\[ \theta_2 = -i\phi \sqrt{(\kappa_2 + q\epsilon_2)} e^{i(\omega t + \epsilon)}. \]

The corresponding real solution is
\[ \theta_1 = 2\phi \sqrt{(\kappa_1 + q\epsilon_1)} \cos (\lambda t + \epsilon), \]
\[ \theta_2 = 2\phi \sqrt{(\kappa_2 + q\epsilon_2)} \sin (\lambda t + \epsilon). \]

The angular displacements about \( O\xi, O\eta \) are therefore
\[ \theta_1 \cos \omega t - \theta_2 \sin \omega t = \phi \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} + \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \cos [(\omega + \lambda) t + \epsilon] \]
\[ + \phi \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} - \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \cos [(\omega - \lambda) t - \epsilon], \]
\[ \theta_2 \cos \omega t + \theta_1 \sin \omega t = \phi \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} + \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \sin [(\omega + \lambda) t + \epsilon] \]
\[ + \phi \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} - \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \sin [(\omega - \lambda) t - \epsilon]. \]

The motion of the principal axis in space consists, therefore, of a combination of two simple harmonic motions, the period of each being approximately equal to the period of rotation of the system, and the amplitudes being in the ratio \( \sqrt{(\kappa_1 + q\epsilon_1)} : \sqrt{(\kappa_2 + q\epsilon_2)} : \sqrt{(\kappa_1 + q\epsilon_1)} + \sqrt{(\kappa_2 + q\epsilon_2)} \); in virtue of each of these oscillations, the principal axis will describe a cone of revolution in the direction in which the system is rotating. In the event of the system being symmetrical about the axis of rotation \( \kappa_1 = \kappa_2 \) and \( \epsilon_1 = \epsilon_2 \), in this case the amplitude of one of the oscillations reduces to zero.

We have likewise
\[ \frac{\dot{\theta}_1}{\omega} = -2\phi \frac{\lambda}{\omega} \sqrt{(\kappa_1 + q\epsilon_1)} \sin (\lambda t + \epsilon), \]
\[ \frac{\dot{\theta}_2}{\omega} = +2\phi \frac{\lambda}{\omega} \sqrt{(\kappa_2 + q\epsilon_2)} \cos (\lambda t + \epsilon), \]
\[ \frac{\dot{\theta}_1}{\omega} \cos \omega t - \frac{\dot{\theta}_2}{\omega} \sin \omega t = -\phi \frac{\lambda}{\omega} \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} + \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \sin (\omega + \lambda) t + \epsilon \]
\[ -\phi \frac{\lambda}{\omega} \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} - \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \sin (\omega - \lambda) t - \epsilon, \]
\[ \frac{\dot{\theta}_1}{\omega} \sin \omega t + \frac{\dot{\theta}_2}{\omega} \cos \omega t = \phi \frac{\lambda}{\omega} \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} + \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \cos [(\omega + \lambda) t + \epsilon] \]
\[ +\phi \frac{\lambda}{\omega} \left\{ \sqrt{(\kappa_1 + q\epsilon_1)} - \sqrt{(\kappa_2 + q\epsilon_2)} \right\} \cos [(\omega - \lambda) t - \epsilon]. \]

The motion of the instantaneous axis of rotation of the shell is therefore in all respects similar to that of the principal axis, but the semi-vertical angles of the cones described are smaller in the ratio \( \lambda : \omega \).

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ON THE OSCILLATIONS OF A ROTATING ELLIPSOIDAL SHELL.

The direction-cosines of the instantaneous axis referred to the principal axes of the shell $Ox_1, Oy_1, Oz_1$ are

$$
\begin{align*}
\dot{\theta}_1 &= -\omega \theta_2, \\
\dot{\theta}_2 &= +\omega \theta_1,
\end{align*}
$$

or

$$
-2\phi \left[ \frac{\lambda}{\omega} \sqrt{(\kappa_1 + q\epsilon_1) + \sqrt{\kappa_2 + q\epsilon_2}} \right] \sin(\lambda t + \epsilon),
$$

$$
2\phi \left[ \frac{\lambda}{\omega} \sqrt{\kappa_2 + q\epsilon_2} + \sqrt{(\kappa_1 + q\epsilon_1)} \right] \cos(\lambda t + \epsilon),
$$

therefore, relatively to the shell, the instantaneous axis describes a cone in period $2\pi/\lambda$. This motion would ensue if the shell were started rotating about an axis not coincident with its principal axis, and it is analogous to the motion of a rigid body under no forces when slightly disturbed from a motion of pure rotation about a principal axis.
XIII. *On the Velocities of the Ions.*

By W. C. Dampier Whetham, M.A., Fellow of Trinity College, Cambridge.

Communicated by Professor J. J. Thomson, F.R.S.

Received May 2,—Read May 30, 1895.

In a previous communication to the Royal Society (‘Phil. Trans.’ 184 (1893), A, p. 337), I have described a method of experimentally determining the velocities of the ions during electrolysis, by observations on the phenomena at the junction of two salt solutions, one at least of which is coloured, when a current of electricity is passed from one to the other.

For the success of the method it is necessary to choose two solutions which (1) are different in density, (2) different in colour, and (3) have nearly equal conductivities at equivalent concentrations, *i.e.*, when the number of gram-molecules dissolved in 1 litre of solution is the same for both. These conditions seriously restrict the number of cases to which the method is applicable, but the results obtained for copper and for the bichromate group ($\text{Cr}_2\text{O}_7^{\text{2-}}$) agree well with the values theoretically deduced by Kohlrausch from measurements of the conductivity. Alcoholic solutions of cobalt nitrate and chloride were also used, and the sum of the velocities of the opposite ions, in each case, observed in my experiments, was as nearly as could be expected, the same as their sum calculated from the conductivities by Kohlrausch’s method.

In order to extend the method to cases in which there was no colour to be observed, I have returned to the use of solid solutions in agar-agar jelly, by means of which the first direct experimental measurement of the velocity of an ion was made by Dr. Oliver Lodge (‘B.A. Report,’ 1886), who traced the course of the hydrogen ion as it travelled along a tube filled with a jelly solution of sodium chloride, forming hydrochloric acid, and decolorizing phenol-phthalein as it went. Dr. Lodge tried to determine the velocity of other ions, such as barium, by tracing the precipitates which they formed with suitable reagents, but the results were not satisfactory.

The chief objections to the use of precipitates in jelly solutions are (1) the jelly exudes from the tube under the action of the current; (2) the formation of the precipitate withdraws some of the electrolyte from the solution, and hence changes in conductivity result, which alter the potential gradient, or form surfaces separating liquids of different conductivity, over which distributions of electrification will occur.

3 T 2

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The motion of the jelly as a whole is very slow compared with the speed of the ions, and, if we can measure the velocity while the ions are only moving over a small distance in a short time, it need not affect the result by disturbing the experiment in any other way.

In order to test whether trustworthy observations could be made with jelly solutions, I determined the velocity of the bichromate group when travelling through them. Decinormal solutions of potassium bichromate and potassium chloride were used in the manner presently to be described, and the velocity of the \( \text{Cr}_2\text{O}_7^{2-} \) ion under unit potential-gradient (one volt per centimetre) came out 0.00044 centim. per second. In the earlier investigation the same group travelled through an aqueous solution of the same strength with a velocity of 0.00047 centim. per second. The effect of the jelly thus appears to be only slightly to retard the motions. Moreover, \textit{Arrhenius} has shown ("\textit{B.A. Report}," 1886, p. 344) that the viscosity of jelly solutions has but a small influence on the conductivity.

The alteration in concentration, due to the formation of a precipitate, appears to have been very considerable in Dr. \textit{Lodge}'s experiments, and may explain his uncertain results. It can, however, be made very small in the following way. Instead of setting up, in contact with each other, two solutions, like barium chloride and sodium sulphate, which completely precipitate each other, the solutions used were barium chloride and sodium chloride, just enough sodium sulphate being added to the latter to enable the motion of the barium ions to be traced by watching the formation of a slight precipitate of barium sulphate. That this did not seriously affect the result was shown by repeating the experiment with less sodium sulphate. The specific ionic velocity then came out 0.000386 centim. per second, a number agreeing with that first obtained, 0.000390, quite as well as the unavoidable errors of experiment would lead us to expect.

The use of jelly solutions, and of precipitates as indicators, being thus justified, many ions could be examined which could not have had their velocity determined by means of a colour boundary. \textit{Kohlrausch} has lately given corrected values for a number of ionic velocities ("\textit{Wied. Ann.}," 1893, vol. 50, p. 385), and, in some cases, tabulated them for solutions of various concentrations. It was, therefore, convenient to determine some of these, and barium, calcium, silver and the \( \text{SO}_4^{2-} \) group, present in sulphates, were chosen as convenient examples.

The apparatus used and the method of measurement were the same as those of the former investigation.

Two vertical glass tubes, about 2 centims. in diameter, were joined by a third, considerably narrower, which was bent parallel to the others for the greater part of its length. One jelly solution was melted and poured into the longer limb till it about half filled it, and was allowed to cool and solidify. The other solution was then poured into the shorter limb, and, when it was solid, the whole was placed in a glass water-bath in front of a window, with a transparent glass scale fixed behind
the junction tube. A precipitate formed at the surface of contact between the two solutions, and, when a current was passed from one platinum electrode to the other, the precipitate gradually spread upward or downwards with a velocity which could be measured on the scale by means of a telescope.

If the potential gradient at the junction is $dV/dx$, we have

$$dV/dx = \gamma r/A,$$

where $\gamma$ represents the total current, $r$ the specific resistance of the solution, and $A$ the area of cross-section of the tube.

If $v$ be the observed velocity, the specific velocity for unit potential gradient is given by

$$v_1 = \frac{v}{dV/dx} = \frac{vA}{\gamma r}.$$

$A$ is determined by filling a known length of the tube with water or mercury, $\gamma$ is read off on a galvanometer previously graduated, and $r$ is determined by Kohlrausch's method of a Wheatstone's bridge with alternating currents. In order that the method should be a success, it is necessary that the solutions should be of nearly equal specific resistance, so that a mean value of $r$ may be taken. The slight disturbing effect of any small difference is shown in the former paper to be eliminated if measurements be made when the current is passing in both directions, and the mean taken. But, unlike the colour boundary method, the formation of a precipitate is an irreversible process, so that measurements of the velocity can only be made when the current passes in one direction. All that can be done is to choose solutions of
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nearly equal specific resistance, so that the uncertainty, which must appear in the result, shall be, at all events, as small as possible.

**Barium.**—Decinormal solutions of sodium chloride and barium chloride, the former containing a little sodium sulphate, were made up with agar jelly just strong enough to set. The resistance of each was determined in a cell of the form shown in fig. 2,

![Figure 2](image)

the constant of which was known, and gave the conductivity of any solution in reciprocals of legal ohms, by dividing 1.5596 by the observed resistance measured in legal ohms.

Resistances of solutions:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Resistance (ohms)</th>
<th>Conductivity (recip. ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>15°8 = 161.8</td>
<td></td>
</tr>
<tr>
<td>Barium</td>
<td>13°4 = 173.0</td>
<td></td>
</tr>
</tbody>
</table>

The temperature coefficient of resistance is, therefore, about 2.5 per cent. per degree, and the mean conductivity of the two solutions at 15°8, 9.60 \times 10^{-3}.

A small tangent galvanometer was adjusted and graduated by passing the current from a freshly prepared Daniell's cell through it and a box of resistance coils arranged in series. The following readings were obtained—

<table>
<thead>
<tr>
<th>Resistance (ohms)</th>
<th>Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>21.6</td>
</tr>
<tr>
<td>240</td>
<td>22.1</td>
</tr>
<tr>
<td>230</td>
<td>22.9</td>
</tr>
<tr>
<td>220</td>
<td>23.8</td>
</tr>
<tr>
<td>210</td>
<td>24.5</td>
</tr>
<tr>
<td>200</td>
<td>25.4</td>
</tr>
<tr>
<td>190</td>
<td>26.4</td>
</tr>
<tr>
<td>180</td>
<td>27.5</td>
</tr>
<tr>
<td>170</td>
<td>28.7</td>
</tr>
<tr>
<td>160</td>
<td>29.8</td>
</tr>
<tr>
<td>150</td>
<td>31.3</td>
</tr>
<tr>
<td>140</td>
<td>32.7</td>
</tr>
<tr>
<td>130</td>
<td>34.5</td>
</tr>
<tr>
<td>120</td>
<td>36.1</td>
</tr>
<tr>
<td>110</td>
<td>38.4</td>
</tr>
<tr>
<td>100</td>
<td>40.6</td>
</tr>
</tbody>
</table>

The resistance of the galvanometer and its leads was 10 ohms.

* A decinormal solution contains one-tenth of the equivalent weight of the substance in grams in one litre of solution, e.g., \(1 \times \frac{1}{9} \text{BaCl}_2 = 1 \times \frac{1}{9} (137 + 70.8) = 10.39\) grams per litre.
The solutions were then placed in the velocity apparatus, and measurements taken, the temperature of the water bath being 15°8.

<table>
<thead>
<tr>
<th>Time</th>
<th>Galvanometer</th>
<th>Scale reading</th>
<th>Displacement in 10 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.14</td>
<td>35.8</td>
<td>24.39</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>24.28</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>&quot;</td>
<td>24.20</td>
<td></td>
</tr>
<tr>
<td>11.24</td>
<td>35.9</td>
<td>23.93</td>
<td>0.46</td>
</tr>
<tr>
<td>26</td>
<td>&quot;</td>
<td>23.83</td>
<td>0.45</td>
</tr>
<tr>
<td>28</td>
<td>&quot;</td>
<td>23.75</td>
<td>0.45</td>
</tr>
<tr>
<td>11.34</td>
<td>36.0</td>
<td>23.50</td>
<td>0.43</td>
</tr>
<tr>
<td>35</td>
<td>&quot;</td>
<td>23.40</td>
<td>0.43</td>
</tr>
<tr>
<td>38</td>
<td>&quot;</td>
<td>23.30</td>
<td>0.45</td>
</tr>
<tr>
<td>11.44</td>
<td>36.0</td>
<td>23.05</td>
<td>0.45</td>
</tr>
<tr>
<td>46</td>
<td>&quot;</td>
<td>22.95</td>
<td>0.45</td>
</tr>
<tr>
<td>48</td>
<td>&quot;</td>
<td>22.86</td>
<td>0.44</td>
</tr>
<tr>
<td>11.54</td>
<td>36.0</td>
<td>22.60</td>
<td>0.45</td>
</tr>
<tr>
<td>56</td>
<td>&quot;</td>
<td>22.51</td>
<td>0.44</td>
</tr>
<tr>
<td>58</td>
<td>&quot;</td>
<td>22.41</td>
<td>0.45</td>
</tr>
<tr>
<td>12.4</td>
<td>36.2</td>
<td>22.16</td>
<td>0.44</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>22.05</td>
<td>0.46</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>21.98</td>
<td>0.43</td>
</tr>
<tr>
<td>12.14</td>
<td>36.3</td>
<td>21.71</td>
<td>0.45</td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>21.61</td>
<td>0.44</td>
</tr>
<tr>
<td>18</td>
<td>&quot;</td>
<td>21.52</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The velocity of the junction thus kept constant throughout. Its mean value is 0.446 centim. in 10'. The mean galvanometer reading is 36.0, which indicates a current equal to that produced by the electromotive force of one Daniell (= 1.08 volt) working through a resistance of $121 + 10 = 131$ ohms. The area of cross section of the tube is 0.430 square centim., and $r$ is the reciprocal of $9.60 \times 10^{-2}$. We thus get

$$v_1 = \frac{vA}{r} = \frac{0.446 \times 0.430 \times 131 \times 9.60 \times 10^{-3}}{10 \times 60 \times 1.08} = 0.000372 \text{ centim. per second.}$$

Experiments presently to be described gave for the temperature coefficient of the velocity the values 2.78 per cent. at 15°7, and 2.05 per cent. at 12°8. The mean of these 2.4 is very near the value, 2.5, found for the temperature coefficient of the conductivity, and justifies us in using the latter value for the small correction necessary to reduce the observations to 18°, the temperature for which Kohlrausch's numbers are calculated.
We thus find for the specific ionic velocity of the barium ion, travelling through a decinormal solution of barium chloride in solid agar jelly at a temperature of $18^\circ$,

$$v_{Ba} = 0.000393 \text{ centim. per sec.}$$

For an aqueous solution of corresponding strength, Kohlrausch calculates, that, in order to give the observed values to the conductivity and the migration constant, the barium ion must have a specific velocity of

$$v_{Ba} = 0.000366 \text{ centim. per sec.}$$

New solutions were then set up, the amount of sodium sulphate being only just enough to give a visible precipitate. The voltage used was less—about 24 instead of 40, but otherwise the experiments were similar.

The following mean results were obtained:

$$v = 0.244 \text{ centim. in 10 mins.}$$


Therefore

$$v_1 = 0.000376 \text{ centim. per sec.},$$

which gives for the velocity of the barium ion at $18^\circ$ the value

$$v_{Ba} = 0.000386 \text{ centim. per sec.}$$

_Calcium._—The determination of the velocity of the calcium ion was not quite so satisfactory. The solutions used were decinormal ones of calcium chloride and sodium chloride, sodium carbonate being added to the latter as indicator. The precipitate of calcium carbonate was only visible when a considerable amount of sodium carbonate was present. This would make the change in concentration, due to the precipitation, considerable, and tend to increase the potential gradient at the boundary, and make the observed velocity greater.

The galvanometer had been moved, so that it was re-graduated.

<table>
<thead>
<tr>
<th>Resistance (ohms)</th>
<th>Galvanometer</th>
<th>Resistance (ohms)</th>
<th>Galvanometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>27.5</td>
<td>150</td>
<td>31.5</td>
</tr>
<tr>
<td>170</td>
<td>29.3</td>
<td>140</td>
<td>33.5</td>
</tr>
<tr>
<td>160</td>
<td>30.1</td>
<td>130</td>
<td>35.1</td>
</tr>
</tbody>
</table>

To these resistances 10 ohms must be added for the galvanometer and leads.
Resistance of calcium chloride solution in cell at $18^\circ = 180$ ohms.

sodium $\ldots = 170$

Mean conductivity $= 8.91 \times 10^{-3}$.

The junction moved the following distances in 10 mins.:

$0.38, 0.38, 0.39, 0.38, 0.36, 0.38, 0.38, 0.40, 0.36, 0.36, 0.36$.

Mean $= 0.376$ centim. Mean galvanometer reading $32.9$. Therefore $\gamma = 1.08/153$.

Temperature of water bath $= 18^\circ$. Area of tube $= 0.442$.

Therefore $v_1 = 0.000350$ centim. per sec.,

which gives for the specific velocity of the calcium ion, moving through a decinormal solution of calcium chloride in agar jelly at $18^\circ C$, the value

$v_{Ca} = 0.000349$ centim. per sec.

For the corresponding aqueous solution Kohlrausch gives

$v_{Ca} = 0.000290$ centim. per sec.

The temperature coefficient of the velocity was determined for these solutions by cooling the water-bath to $13^\circ.2$.

Mean conductivity at $13^\circ.2 = 7.90 \times 10^{-3}$.

Velocity $= 0.34, 0.30, 0.34, 0.32, 0.34, 0.32, 0.32, 0.32, 0.32$. Mean $= 0.324$ centim. in 10 mins.

Mean galvanometer reading $= 29.7$. Therefore $\gamma = 1.08/175$.

Therefore $v_1 = 0.000305$ centim. per sec.,

which gives a temperature coefficient, at a mean temperature of $15^\circ.7$, of 2.78 per cent. per degree.

Silver.—Decinormal jelly solutions of silver nitrate and sodium nitrate, the latter containing a little sodium chloride, gave in the resistance cell

Silver nitrate at $17^\circ.4 = 171$ ohms.
Sodium $\ldots, 17^\circ.4 = 177$

Therefore mean conductivity at $17^\circ.4 = 8.96 \times 10^{-3}$.
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Mean galvanometer reading = 31.0. Therefore $\gamma = 1.08/164$.
Temperature of water-bath, 17°.4. Area of cross-section of tube = 0.442 square centim.
Therefore

$$v_1 = 0.000481 \text{ centim. per sec.}$$

Thus the specific velocity of the silver ion, moving through a decinormal solution of silver nitrate in agar jelly at 18°, is

$$v_{Ag} = 0.000488 \text{ centim. per sec.}$$

For the corresponding solution in water, Kohlrausch gives

$$v_{Ag} = 0.000462 \text{ centim. per sec.}$$

The temperature coefficient was determined by cooling the water-bath to 8°.2.
Mean conductivity at 8°.2 = 7.12 × $10^{-3}$.
The electromotive force applied being the same as before, we can compare this with 0.480 centim. in 10 mins., the velocity at 17°.4. The temperature coefficient at the mean temperature of 12°.8 is thus 2.05 per cent. per degree.

The Sulphate Group.—As an example of an anion the velocity of the $SO_4^-$ group was determined by the use of decinormal jelly solutions of sodium sulphate and sodium chloride, barium chloride being added to the latter as indicator.
The galvanometer was re-graduated, the following readings being enough for our purpose. To the resistances 10 ohms must be added for the galvanometer.

<table>
<thead>
<tr>
<th>Resistance (ohms)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>80</td>
<td>47</td>
</tr>
<tr>
<td>230</td>
<td>23</td>
</tr>
<tr>
<td>250</td>
<td>22</td>
</tr>
</tbody>
</table>

Resistance of sodium chloride solution in cell at 14°.6 = 151.5.
Therefore mean conductivity at 15°.2 = 9.69 × $10^{-3}$.
Mean galvanometer reading = 23.3. Therefore $\gamma = 1.08/246$.
Temperature 15°.2. Area of cross-section of tube = 0.430 square centim.
Therefore

$$v_1 = 0.000406 \text{ centim. per sec.}$$
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This gives for the specific ionic velocity of the SO$_4$ ion, when travelling through a decinormal solution of sodium sulphate in agar jelly at 18°,

$$V_{SO_4} = 0.000434 \text{ centim. per sec.}$$

Kohlrausch finds for decinormal potassium sulphate solution in water

$$V_{SO_4} = 0.000492 \text{ centim. per sec.}$$

Another determination was then made in another tube having a larger area of cross-section = 0.746 sq. centim.

Temperature 11°.3. Mean conductivity = 8.79 x 10$^{-3}$. Velocity = 0.38, 0.40, 0.41, 0.44, 0.47, 0.44, 0.48, 0.44, 0.42, 0.44, 0.44, 0.50. Mean = 0.438 centim. in 10 mins.

Mean galvanometer reading = 48°.4. Therefore $\gamma = \frac{1.08}{77.5 + 10}$.

Therefore

$$V_1 = 0.000388 \text{ centim. per sec.},$$

which at 18° gives us

$$V_{SO_4} = 0.000458 \text{ centim. per sec.}$$

The numbers thus obtained all agree with those deduced from theory, to an accuracy which must be considered to be as great as the unavoidable experimental errors would lead us to expect.*

Certain substances, such as ammonia and acetic acid, are known to have abnormally low conductivities, as long, at all events, as the aqueous solutions containing them are not exceedingly dilute. It seemed of great interest to examine whether the velocities were, in these cases, proportionately reduced. The result of an investigation on acetic acid, in which phenol-phthallein was used as indicator, has already been published (‘Philosophical Magazine,’ October, 1894), and gave the velocity of the hydrogen ion travelling through an agar jelly solution containing 0.07 gram.-equivalent of sodium acetate per litre, as

$$V_{H^+} = 0.000065 \text{ centim. per sec.}$$

Now the value given by Kohlrausch for the specific velocity of the hydrogen ion in a solution of hydrochloric acid of this concentration is

$$V_{H^+} = 0.0030 \text{ centim. per sec.},$$

so that, when travelling through acetates, its speed is reduced in the ratio of 1 to 46.

* It is worthy of remark that the velocities of all the kations measured come out larger than theory requires, while that of the one anion (SO$_4$) comes out less. It is possible that this may be due to the presence of the jelly.
The ratio of the conductivity of a solution of acetic acid, containing 0'07 gram-equivalent per litre, to that of an equivalent solution of hydrochloric acid is 1 to 62. Thus the velocity of the hydrogen ion is reduced in about the same proportion as the conductivity.

In order to examine the velocity of the acetate ion (C₂H₃O₂) of acetic acid, some substance was needed to serve as indicator. With ferric salts, acetates give a deep red colour, which is also produced if the solid ferric acetate is dissolved in water.

It is well known that solutions of ferric chloride undergo decomposition into soluble ferric hydroxide and hydrochloric acid, to an amount which increases as the dilution gets greater, and as the temperature rises. The hydrochloric acid can, in fact, be separated from the hydroxide of iron by dialysis through a membrane of parchment paper.

The electrical conductivity of an aqueous solution of ferric acetate shows that, in this case also, a similar reaction goes on, for it has an abnormally low conductivity, comparable with that of equivalent solutions of acetic acid, just as a solution of ferric chloride has an abnormally great conductivity owing to the presence of hydrochloric acid.

The molecular conductivity of an aqueous solution of ferric acetate, containing one-tenth of a gram-equivalent of iron in one litre, was determined by measuring its resistance in another cell, whose constant was found by filling it with standard solutions of silver nitrate and barium chloride. The conductivity of any solution could be found by dividing the constant, 1'604 × 10⁻³, by its observed resistance in legal ohms. A volume of 10 cub. centims. of this solution was then taken, and made up to 100 cub. centims. in a graduated flask.

This process was repeated three times, with the following results:—The first column, headed n, gives the concentration of the solution in gram-equivalents of iron per litre; the second, R, gives the observed resistance in the cell; the third, T, shows the temperature; in the fourth are put the values of k₀, the conductivity in C.G.S. units, that of the water being subtracted, reduced to a temperature of 18°, and the fifth gives k₀/n, the molecular conductivity.

<table>
<thead>
<tr>
<th>n</th>
<th>R</th>
<th>T</th>
<th>k₀ at 18°</th>
<th>k₀/n at 18°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2455</td>
<td>16'3</td>
<td>7'03 × 10⁻¹²</td>
<td>70'3 × 10⁻¹³</td>
</tr>
<tr>
<td>0'1</td>
<td>2'180</td>
<td>21'2</td>
<td>1'25 × 10⁻¹²</td>
<td>12'5 &quot;</td>
</tr>
<tr>
<td>0'01</td>
<td>1'280</td>
<td>17'9</td>
<td>2'99 × 10⁻¹¹</td>
<td>29'9 &quot;</td>
</tr>
<tr>
<td>0'001</td>
<td>4'9700</td>
<td>17'7</td>
<td>6'74 × 10⁻¹³</td>
<td>67'4 &quot;</td>
</tr>
<tr>
<td>0'001</td>
<td>177000</td>
<td>16'6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For equivalent solutions of acetic acid, Kohlrausch ('Wied. Ann.', 26, p. 197) gives the following results:—
It is, therefore, probable that, just as ferric chloride decomposes into ferric hydroxide and hydrochloric acid, thus:

$$\text{FeCl}_3 + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{HCl},$$

so ferric acetate gives ferric hydroxide and acetic acid, thus:

$$\text{Fe(C}_2\text{H}_3\text{O}_2)_3 + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3(\text{H.C}_2\text{H}_3\text{O}_2).$$

In each case most of the work of carrying the current is done by the acid.

An attempt was made to use the red colour of the ferric acetate as an indicator to show the presence of the acetate group. A decinormal solution of ferric chloride was placed in one limb of the apparatus, and a similar solution, coloured red by a little ferric acetate, in the other. It was thought that, by the motion of the colour boundary, the acetate group could be traced, and, since the current is almost exclusively carried by the free acid, that the velocity thus measured would be that of the anion of acetic acid in dilute solution.

When the current was applied, however, it was at once seen that the colour boundary moved in the same direction as the current—not against it as an anion should. The following measurements were obtained:

Resistance of ferric chloride solution in a third cell at $18^\circ\cdot8 = 363$ ohms.

" " " + acetate solution in Cell No. 2 at $18^\circ\cdot9 = 384\cdot5$ ohms.

Cell constant = 2.356.

Therefore mean conductivity at $19^\circ\cdot2 = 6\cdot35 \times 10^{-3}$.

Velocity.—Half-hour intervals. Current upwards. Displacement upwards:


Current downwards. Displacement downwards:

'9, '9, '9, '8, '8, '8.

Mean velocity = 0.833 centim. in 30 minutes.

Mean galvanometer reading = $46^\circ\cdot2$. Resistance of galvanometer = 218 ohms.

Graduation with a Daniell cell:
therefore \[ \gamma = 1.08/243, \]
therefore \[ v_1 = -0.000284 \text{ centim. per second,} \]
which, reduced to 18°, gives
\[ -0.000276 \text{ centim. per second.} \]

If this really represents the velocity of the acetate group in an acid solution, it is
evident that, if a measurement be made of the migration constant of acetic acid, the
concentration round the kathode must increase, since the acetate group travels in the
same direction as the hydrogen.

The current from twenty storage cells was passed for some hours through a deci-
normal solution of acetic acid. The liquid was contained in an apparatus consisting
of two upright glass tubes, in which the platinum electrodes were placed. These
tubes were connected below the level of the top of the solution by a horizontal tube,
made of india-rubber for part of its length, in order that it might be closed by a
screw pinch-cock. After the passage of the current, the two vessels could thus be
isolated from each other, and the contents of each examined.

A current of 0.0014 ampère was passed for 5 hours, at the end of which time the
solution round each electrode was titrated with decinormal soda solution with the
following results:

<table>
<thead>
<tr>
<th>Original solution</th>
<th>. . . 10 cub. centims. require 10.0 cub. centims. soda.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>. . . &quot; &quot; 10.4 &quot; &quot;</td>
</tr>
<tr>
<td>Kathode</td>
<td>. . . &quot; &quot; 9.9 &quot; &quot;</td>
</tr>
</tbody>
</table>

This preliminary observation, therefore, gives no evidence of accumulation of acid
at the kathode.

The experiment was repeated. A current, whose average strength was 0.00178
ampère, was passed through decinormal acetic acid solution for 38\frac{1}{2} hours.

<table>
<thead>
<tr>
<th>Original solution</th>
<th>. . . 10 cub. centims. require 9.8 cub. centims. soda.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>. . . &quot; &quot; 9.85 &quot; &quot;</td>
</tr>
<tr>
<td>Kathode</td>
<td>. . . &quot; &quot; 9.4 &quot; &quot;</td>
</tr>
</tbody>
</table>

Now it is possible that an accumulation round the kathode might be masked by
the reduction of the acetic acid by the hydrogen there liberated, but, if such an
accumulation occurred, it would mean that all the acid decomposed must be taken
from the anode vessel, as well as some which migrates unchanged through the liquid.
The numbers given above seem to show conclusively that the amount of acid round
the anode does not decrease, but that, if anything, a slight increase occurs.
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OF THE

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FOR THE YEAR 1895.

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We must, therefore, look for some other explanation of the velocity phenomena. If ferric hydrate be dissolved in ferric chloride solution, a red liquid is obtained. When it is remembered that the ferric acetate solution contains ferric hydrate, it is evident that a motion of the colour boundary would be obtained if this ferric hydrate were carried through the solution, either by its being attached to the kation, or by a motion similar to that observed in the case of light non-electrolytic particles suspended in water.

Ferric hydrate can be obtained in a soluble form by dialysing a solution of ferric chloride. The ferric chloride solution is placed in a glass cylinder, the lower end of which is covered by a sheet of parchment paper. The cylinder is then suspended in such a manner that the lower end is just below the surface of a large volume of distilled water. At the end of several days, nearly all the hydrochloric acid is found to have passed into the water, leaving the iron behind as a brown solution of ferric hydrate. A solution prepared in this manner was found to have a concentration of 0.0044 gram-equivalent per litre of chlorine, and 0.0652 gram-equivalent of total iron. Its conductivity was, in C.G.S. units, $7.83 \times 10^{-13}$, which gives for the iron a molecular conductivity of $120 \times 10^{-13}$, a value much below the normal. If, however, we suppose that it is only the ferric chloride remaining in the solution which is active, and calculate the molecular conductivity from the amount of chlorine, we get $1780 \times 10^{-13}$—a number nearly equal to that for the ordinary ferric chloride solution of equivalent strength.

A series of conductivity measurements of this solution was made at different dilutions, and then two similar sets for ferric chloride. In the following Table the results are compared.

<table>
<thead>
<tr>
<th>Concentration in gram.-equivalents of chlorine per litre.</th>
<th>Molecular conductivity at 18°.</th>
<th>Concentration in gram.-equivalents per litre.</th>
<th>Molecular conductivity at 18°.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0044</td>
<td>$1780 \times 10^{-13}$</td>
<td>0.000068</td>
<td>$1445 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.00088</td>
<td>2255</td>
<td>0.000353</td>
<td>2575</td>
</tr>
<tr>
<td>0.000176</td>
<td>2580</td>
<td>0.000131</td>
<td>2690</td>
</tr>
<tr>
<td>0.0000352</td>
<td>1267</td>
<td>0.000068</td>
<td>2747</td>
</tr>
<tr>
<td>0.0000176</td>
<td>1016</td>
<td>0.0000506</td>
<td>2250</td>
</tr>
<tr>
<td>0.0000068</td>
<td></td>
<td>915</td>
<td></td>
</tr>
</tbody>
</table>

The molecular conductivities are corrected for the conductivity of the re-distilled water used ($2.97 \times 10^{-15}$), and reduced to 18°.
The two series of numbers correspond with each other within the limits of experimental error, and this indicates that the conductivity of the solution of dialysed iron is due, in great part, at any rate, to the presence of residual chloride. Whether the conductivities of these two solutions are accurately equal or not, it would need a thorough investigation to decide, and this was unnecessary for the immediate purposes of this paper. One would imagine that, if the conduction is entirely done by the chloride, the conductivity of the dialysed iron solution would be a little reduced, for the residual chloride, finding itself in presence of a large excess of ferric hydroxide, one of the products of its decomposition, would be less completely resolved into hydroxide and acid than in its ordinary solutions, and would, therefore, have a molecular conductivity more nearly equal to that of common salts than in the usual case.

It is interesting to observe that the molecular conductivity, in both these cases, reaches a maximum as the concentration decreases, and then, as the dilution is pushed still further, again falls. This is a characteristic property of the solutions of free acids and alkalis, and confirms the hypothesis that decomposition into ferric hydroxide and hydrochloric acid occurs. We may take it, then, that the ferric hydroxide, into which solutions of iron salts are partially decomposed, is electrolytically nearly inactive, the conductivity being almost entirely due to the acid formed. It is the large quantity of this hydroxide present that gives the dark red colour to ferric acetate solutions, and it is the motion of the ferric hydroxide which is measured by observations on the movement of the colour boundary in the velocity experiment.

In order to examine this conclusion, 10 cub. centims. of a solution of ferric chloride were run into some dialysed iron solution, and made up to 100 cub. centims. Another volume of 10 cub. centims. of the same ferric chloride was made up to 100 cub. centims. with water. These two solutions were placed in the velocity apparatus, and a measurement of the velocity of the red colour boundary made. It travelled in the same direction as the current.

Resistance of ferric chloride in cell, 818 ohms at 18°-4.

, , 

+ hydroxide, 607 ohms at 16°-8.

Mean conductivity in reciprocals of legal ohms at 16°-2 = 2·12 × 10⁻³.


64, 63, 65, 65, 68, 64.

Current downwards. Downward displacement during successive intervals of 10 minutes.

81, 81, 77, 69, 67, 66, 68, 70, 66.

The first three measurements of the latter series are much larger than the rest,
and after them the velocity kept constant. It is probable that the extra value was
due to some disturbance at the boundary introduced by the first current, which
gradually got reversed and eliminated when the current was reversed. These three
observations were therefore neglected. The others give a mean velocity of 0.68 centim.
in 10 minutes. We thus get for the velocity with which ferric hydroxide is trans-
ported in the direction of the current through a dilute solution of ferric chloride, by a
potential gradient of 1 volt per centim., at a temperature of 16°-2, the value
0.000315 centim. per second, and at 18°

0.00033 centim. per second.

This is the same, within the limits of experimental error (which with these badly
cconducting solutions are considerable) as the value deduced by experiments with
ferric acetate solutions of rather greater concentration, which was

0.00028 centim. per second.

It seems clear, then, that what we were measuring in that case, was not the
velocity of the acetate group, but the velocity with which the soluble ferric hydroxide
was transported through the solution without undergoing any decomposition.

In order further to examine this explanation, a migration experiment was made with
the dialysed iron solution. A current of 0.003 ampère was passed through the liquid
for five hours, at the end of which time the red colour had become much paler round
the anode, while a precipitate of ferric hydroxide appeared at the bottom of the vessel
containing the kathode.

The volume of liquid in each vessel was 30 cub. centims., and in 30 cub. centims. of
the original solution the weight of ferric oxide was 0.0780 gram.

In the anode vessel the weight of oxide in solution was 0.0438 gram.

The kathode vessel contained 0.0720 gram. in solution, and 0.0158 gram. precipi-
tated; total, 0.0878 gram.

Thus the anode vessel contains less iron, and the kathode vessel more, than an
equal volume of the original solution. This, also, is consistent with the hypothesis
that unaltered ferric hydroxide is carried through the liquid in the direction of the
current.

A similar experiment, made with ferric acetate solution, also showed an accumulation
of iron in solution near the kathode, both as estimated by the colour of the liquid,
and as determined by analysis.

Our attempt to measure directly the velocity of the acetate group (C₆H₅O₂) in acetic
acid solutions has therefore failed, but the migration experiment, described on p. 518,
at any rate showed that no great change of concentration occurred in the neighbour-
hood of the anode, towards which the acetate group travelled. Its velocity is, there-
for, very small, and, as in the case of common mineral acids, the conductivity is chiefly due to the motion of the hydrogen.

The following table gives the velocities of all ions which have been experimentally determined.

<table>
<thead>
<tr>
<th>Name of ion</th>
<th>Specific ionic velocity in centims. per second</th>
<th>Observer.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated from Kohlraush's theory.</td>
<td>Directly observed.</td>
</tr>
<tr>
<td>Hydrogen (in chlorides)</td>
<td>0.0028</td>
<td>0.0026</td>
</tr>
<tr>
<td>&quot; (in acetates)</td>
<td>0.000048</td>
<td>0.000065</td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td>0.00031</td>
</tr>
<tr>
<td>Bichromate group (Cr₂O₇⁻)</td>
<td>0.00047</td>
<td>0.00047</td>
</tr>
<tr>
<td>Barium</td>
<td>0.00037</td>
<td>0.00039</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.00029</td>
<td>0.00035</td>
</tr>
<tr>
<td>Silver</td>
<td>0.00046</td>
<td>0.00049</td>
</tr>
<tr>
<td>Sulphate group (SO₄²⁻)</td>
<td></td>
<td>0.00045</td>
</tr>
<tr>
<td>Cobalt (in alcoholic CoCl₂)</td>
<td></td>
<td>0.000022</td>
</tr>
<tr>
<td>&quot;  (Co(NO₃)₂)</td>
<td></td>
<td>0.000044</td>
</tr>
<tr>
<td>Chlorine (in alcoholic CoCl₂)</td>
<td></td>
<td>0.000026</td>
</tr>
<tr>
<td>Nitrate group (NO₃⁻) (in alcoholic Co(NO₃)₂)</td>
<td></td>
<td>0.000035</td>
</tr>
</tbody>
</table>

The values in the second column are calculated from Kohlraush's theory for solutions of the same concentration as those used for the direct observations. Lodge does not give the strength of his solution, but, as the molecular conductivity of dilute hydrochloric acid does not alter much with change of concentration, the number given, which is calculated for a decinormal solution, is, probably, fairly comparable with that observed. The velocity of copper was measured in chlorides, and the data for the calculation from theory are not known for this salt. The specific ionic velocity of copper, at infinite dilution, is given by Kohlraush as 0.00031 centim. per second. The sum of the ionic velocities of cobalt chloride in alcohol, as calculated from the conductivity of the solution, is 0.000060 centim. per second, and that of cobalt nitrate is 0.000079. These numbers are to be compared with the sums of the observed velocities given in the table, namely, 0.000048 and 0.000079 respectively.

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Introduction.

§ 1. This paper is an attempt to show how the singular solutions of simultaneous ordinary differential equations are to be found either from a complete primitive or from the differential equations.

The latter question has been treated by Mayer (‘Math. Ann.,’ vol. 22, p. 368) in a somewhat different way, but with the same result. He also gives a reference to a paper in Polish by Zajączkowski (summarized in vol. 9 of the ‘Jahrbuch der Fortschritte der Mathematik’), and to one by Serret in vol. 18 of ‘Liouville’s Journal.’

The general result is that there may be as many forms of solution as there are variables (the differential equations being of the first order, to which they may always be reduced). Each form is derived from the one before by the process of finding the envelope, and each contains fewer arbitrary constants by one than the form from which it is directly derived.

The general theory is given in §§ 2, 3, and in § 4 it is shown how the singular solutions are to be formed from the differential equations themselves. In §§ 5–9 the theory is connected with that of consecutive solutions belonging to the complete primitive. §§ 10–13 are taken up with geometrical interpretations relating to plane curves and also to curves in space of \( n + 1 \) dimensions, \( n + 1 \) being the number of variables. In §§ 14–16 the case is discussed in which a system of singular solutions is included in a former system or in the complete primitive.

The rest of the paper contains the application of the theory to certain examples. The first example (§§ 17–21) is the case of the lines in two osculating planes of a twisted curve, and in particular of a twisted cubic. The particular example is given by Mayer and Serret. The second (§§ 22–26) is that of the congruency of common tangents to two quadric surfaces, and generally (§§ 27–35) of the bitangents to any surface. The third (§§ 39–50) is that of the essentially different kind of congruency

\[ 3 \times 2 \]
which consists of the inflexional tangents to a surface. It seems natural to call these two kinds of congruency bitangential and inflexional respectively. The fourth example (§§ 51, 52) is that of a system of conics touching six planes. The fifth (§§ 53–56) is that of a doubly infinite system of parabolas in one plane, the differential equation being a case of an extension of Clairaut’s form \( y = px + f(p) \), which is explained in §§ 53–55.

General Theory. (§§ 2, 3.)

§ 2. Suppose that we have \( n \) ordinary simultaneous differential equations, involving one independent variable \( x \), and \( n \) dependent variables \( y_1, y_2, \ldots, y_n \), with their first differential coefficients \( p_1, p_2, \ldots, p_n \).

The “complete” solution of such a system will consist of \( n \) equations involving \( x, y_1, y_2, \ldots, y_n \), and \( n \) arbitrary constants, \( c_1, c_2, \ldots, c_n \).

Suppose that such a solution is known. The question then arises, “Are there any other solutions which it does not include?” This is the question that we now seek to answer.

If we take the differential equations in the form
\[
J_r(x, y_1, y_2, \ldots, y_n, p_1, \ldots, p_n) = 0 \quad (r = 1, 2, \ldots, n) \quad \ldots \quad (I),
\]
and the integrals as
\[
F_r(x, y_1, \ldots, y_n, c_1, \ldots, c_n) = 0 \quad (r = 1, 2, \ldots, n) \quad \ldots \quad (II),
\]
we have by differentiating
\[
\frac{\partial F_r}{\partial x} + p_1 \frac{\partial F_r}{\partial y_1} + \ldots + p_n \frac{\partial F_r}{\partial y_n} = 0 \quad (r = 1, 2, \ldots, n) \quad \ldots \quad (III).
\]
Let the system
\[
\lambda_r(x, y_1, \ldots, y_n) = 0 \quad (r = 1, 2, \ldots, n) \quad \ldots \quad (IV)
\]
be an integral of (I).

From (IV.) we derive
\[
\frac{\partial \lambda_r}{\partial x} + p_1 \frac{\partial \lambda_r}{\partial y_1} + \ldots + p_n \frac{\partial \lambda_r}{\partial y_n} = 0 \quad (r = 1, 2, \ldots, n) \quad \ldots \quad (V).
\]

By eliminating \( p_1, \ldots, p_n \) from (III.) and (V.) we find such values of \( c_1, c_2, \ldots, c_n \) as will make (III.) and (V.) equivalent*; but if the values of \( p_1, \ldots, p_n \) given by (III.)

* This argument must be somewhat modified if the equations (III.) are not enough to give the values of \( c_1, c_2, \ldots, c_n \). Suppose that \( m \) independent equations, and no more, can be formed from (III.) not containing the quantities \( c_1, \ldots, c_n \). These equations must be included in the system (I.), and are therefore equally satisfied (possibly in virtue of (IV.)) by the values of \( p_1, \ldots, p_n \) given by (V.).

The other \( n - m \) equations of the system (III.) may then be transformed by substitution of the values
and (V.) respectively are substituted in (I.), the results are respectively equivalent to (II.) and (IV.). Hence (II.) and (IV.) are also made equivalent, and therefore (IV.) may be derived from (II.) by substituting appropriate functions of \( x \) for \( c_1, \ldots, c_n \).

Hence, by subtracting (III.) from the derivative of (II.), we have

\[
\sum_{s=1}^{n} \frac{\partial F_s}{\partial c_s} \frac{dc_s}{dx} = 0 \quad (r = 1, 2 \ldots n) \quad \ldots \ldots . \quad (VI.).
\]

Thus, unless \( c_1, c_2 \ldots c_n \) are all constants,

\[
\frac{\partial (F_1, F_2 \ldots F_n)}{\partial (c_1, c_2 \ldots c_n)} = 0 \quad \ldots \ldots \ldots . \quad (VII.).
\]

§ 3. The equations (II.) and (VII.) may be considered as defining \( x, y_1, \ldots y_n \) in terms of \( c_1, c_3 \ldots c_n \), and the equations (VI.) will then give the ratios \( dc_1 : dc_3 : \ldots : dc_n \) in terms of \( c_1, c_3 \ldots c_n \). We thus have \( n - 1 \) differential equations connecting the \( n \) quantities \( c_1, \ldots c_n \). Their complete primitive will involve \( n - 1 \) arbitrary constants, and by eliminating \( c_1 \ldots c_n \) from (II.) and (VII.) and this complete primitive we have a solution of (I.) involving \( n - 1 \) arbitrary constants, which we may call the first singular solution of (I.).

The differential equations given by (VI.) may have a first singular solution involving \( n - 2 \) arbitrary constants, and from this we should derive the second singular solution of (I.) by eliminating \( c_1 \ldots c_n \) as before.

This process may go on till we have \( n \) singular solutions, with \( n - 1, n - 2 \ldots 2, 1, 0 \) arbitrary constants respectively, or it may stop at any stage. If, for instance, the left-hand side of the equation (VII.) were an absolute constant, there would be no singular solution at all.

**Formation of Singular Solutions from the Differential Equations.**

§ 4. The equation (VII.) is the condition that two solutions of (II.) when solved for \( c_1, c_2 \ldots c_n \) shall coincide. But, generally, when this happens, the equations (III.) give coincident sets of values for \( p_1, p_2 \ldots p_n \).

of \( p_1 \ldots p_n \) from (V.), and become relations (A) connecting \( c_1, c_2 \ldots c_n \) with \( x \); and \( y_1, y_2 \ldots y_n \) which are given as functions of \( x \) by (IV.).

Now by substituting the values of \( p_1 \ldots p_n \) from (III.) in (I.), we have integral equations which must be included in (II.).

The number of these equations will be \( n - m \), because \( m \) are already satisfied identically.

These equations are also satisfied if (A) and (IV.) are; for the values of \( p_1 \ldots p_n \) given by (III.) and (V.) are then the same and those given by (V.) satisfy (I.).

The system (II.) will supply exactly \( m \) further equations which in combination with (A) and (IV.) give the values of \( c_1, c_2 \ldots c_n \) in terms of \( x \).
If not, that is if the two sets of values of \( p_1, \ldots \) are different, all the determinants of the matrix

\[
\begin{vmatrix}
\frac{\partial F_1}{\partial x}, & \frac{\partial F_1}{\partial y_1}, & \cdots & \frac{\partial F_1}{\partial y_n} \\
\frac{\partial F_2}{\partial x}, & \frac{\partial F_2}{\partial y_1}, & \cdots & \frac{\partial F_2}{\partial y_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial F_n}{\partial x}, & \frac{\partial F_n}{\partial y_1}, & \cdots & \frac{\partial F_n}{\partial y_n}
\end{vmatrix}
\]

must vanish (compare § 11, below.)

The equations (III.) are then not enough to determine \( p_1, p_2 \ldots p_n \), and the conditions (VI.) do not ensure that the system of equations found by the above process will satisfy (I.) and be a solution at all.

In general, then, for a singular solution, the two sets of values of \( p_1, p_2 \ldots p_n \) are coincident. But these are given by the equations (I.).

Hence generally the equation

\[
\frac{\partial (f_1, f_2, \ldots f_n)}{\partial (p_1, p_2, \ldots p_n)} = 0 \quad \ldots \quad \ldots \quad \ldots \quad (VIII)^*\]

is satisfied by a singular solution.

We have, therefore, the following process for finding the singular solution from the differential equations (I.):

Form the equation (VIII.) and let \( E = 0 \) be the result of eliminating \( p_1, p_2, \ldots p_n \) from (I.) and (VIII.). Suppose that \( \phi \) is a factor of \( E \) such that the equation \( d\phi/dx = 0 \) can be deduced, by substitution without differentiating, from \( \phi = 0 \) and (I.). Then, by treating \( \phi = 0 \) as if it were a particular first integral\(^+\) of (I.), which is now allowable, reduce (I.) to a system of \( n - 1 \) differential equations in \( n \) variables. The complete integral of this system belongs to the first singular solution of (I.). If \( \phi \) is the only factor of \( E \) that satisfies the condition of being an integral, then it yields the whole of the first singular solution.

The first singular solution of the new system of \( n - 1 \) equations gives the second singular solution of the original system of \( n \) equations and so on (see also § 15, below).

\* Mayer finds this equation as the condition that the second and following differential coefficients, as given by the equations (I.), should be indeterminate, and thus shows that (VIII.) must always be satisfied by a singular solution.

\+ If the phrase "first integral" is restricted to such as involve only one arbitrary constant, we may use "singular first integral" for such an equation as \( \phi = 0 \) is here supposed to be.
Analytical Connection of Different Solutions. (§§ 5–9.)

§ 5. Let us write \( J \) for \( \frac{\partial (f_1, f_2, \ldots, f_n)}{\partial (p_1, p_2, \ldots, p_n)} \) and \( \lambda_1, \lambda_2, \ldots, \lambda_n \) for the minors of \( \frac{\partial f_1}{\partial p_1}, \frac{\partial f_2}{\partial p_2}, \ldots, \frac{\partial f_n}{\partial p_n} \) in \( J \).

The equations \( f_1 = 0, f_2 = 0, \ldots, f_n = 0, J = 0 \) give \( p_1, p_2, \ldots, p_n, y_n \) as functions of \( x, y_1, \ldots, y_{n-1}, \) and, for the second singular solution, we have to suppose that two solutions coincide, that is, we put

\[
\frac{\partial (f_1, f_2, \ldots, f_n)}{\partial (p_1, p_2, \ldots, p_n, y_n)} = 0.
\]

Since \( J = 0 \), this equation may be reduced, by multiplication by \( \lambda_x \), to

\[
\left( \lambda_1 \frac{\partial J}{\partial p_1} + \lambda_2 \frac{\partial J}{\partial p_2} + \cdots + \lambda_n \frac{\partial J}{\partial p_n} \right) \frac{\partial (f_1, f_2, \ldots, f_n)}{\partial (p_1, \ldots, p_{n-1}, y_n)} = 0.
\]

Now, \( y_n \) may equally well be replaced by \( y_1, y_2, \ldots, \) or \( y_{n-1} \), so that the condition sought is given by the first factor, which we shall call \( J_1 \).

The equations \( f_1 = 0, \ldots, f_n = 0, J = 0, J_1 = 0 \) give \( p_1, p_2, \ldots, p_n, y_{n-1}, y_n \) as functions of \( x, y_1, \ldots, y_{n-2} \), and, if the values of \( p_{n-1}, p_n \), given by differentiating those of \( y_{n-1}, y_n \), agree with the values given by the solution of the equations, we are to find the second singular solution by integrating the equations that give \( p_1, \ldots, p_{n-2} \).

To find the third singular solution, we have to make the system \( f_1 = 0, \ldots, f_n = 0, J = 0, J_1 = 0 \) have equal roots. The condition for this is found in the same way* to be

\[
\lambda_1 \frac{\partial J}{\partial p_1} + \lambda_2 \frac{\partial J}{\partial p_2} + \cdots + \lambda_n \frac{\partial J}{\partial p_n} = 0,
\]

and so we may pass on to the other singular solutions, if any.

§ 6. As \( J = \lambda_1 \frac{\partial f_n}{\partial p_1} + \lambda_2 \frac{\partial f_n}{\partial p_2} + \cdots + \lambda_n \frac{\partial f_n}{\partial p_n} \), we may write for the integrals that have to be taken to give the \( r \)th singular solution

\[
\left( \sum \lambda \frac{\partial}{\partial p} \right)^s f_n = 0 \quad (s = 1, 2, \ldots, r).
\]

* The condition is

\[
\frac{\partial (f_1, f_2, \ldots, f_n, J_1, J_1)}{\partial (p_1, p_2, \ldots, p_n, y_n, y_{n-1})} = 0.
\]

Multiplied by \( \lambda_x \) this becomes

\[
\sum \lambda \frac{\partial J_1}{\partial p_r} \times \frac{\partial (f_1, \ldots, f_n, J_1, J_1)}{\partial (p_1, \ldots, p_{n-1}, y_n, y_{n-1})} = 0.
\]

The second factor, being unsymmetrical, is irrelevant.
We have also identically
\[(\Sigma \lambda \frac{\partial}{\partial p}) f_i = 0 \quad (i = 1, 2, \ldots n - 1),\]
and therefore
\[(\Sigma \lambda \frac{\partial}{\partial p}) f_i = 0.\]

Thus
\[(\Sigma \lambda \frac{\partial}{\partial p}) (A_1 f_1 + A_2 f_2 + \ldots + A_n f_n) = 0,\]
where \(A_1, A_2, \ldots A_n\) are arbitrary functions.

These may be so chosen that \(\Sigma A f\) is the eliminant of \(f_1, f_2, \ldots f_n\) with respect to \(p_2, \ldots p_n\). We will call this eliminant \(P_1\); it does not involve \(p_2 \ldots p_n\).

The equations then become
\[
\left(\lambda_1 \frac{\partial}{\partial \lambda_1}\right) P_1 = 0 \quad (s = 1, 2, \ldots r),
\]
that is to say
\[
\left(\frac{\partial}{\partial \lambda_1}\right) P_1 = 0 \quad (s = 1, 2, \ldots r).
\]

Thus the equation \(P_1 = 0\) gives \(r + 1\) coincident values of \(p_1\). The same holds for \(p_2, p_3, \ldots p_n\).

If we take a system of values of \(x, y_1, \ldots y_n\) such that \(s\) consecutive members \(^*\) of the \(r\)th singular system of solutions are satisfied, then \(s - 1\) consecutive members of the \((r + 1)\)th will be satisfied, \(s - 2\) of the \((r + 2)\)th and so on to the \((r + s - 1)\)th, after which none are satisfied. Also \(s + 1\) of the \((r - 1)\)th system will be satisfied, \(s + 2\) of the \((r - 2)\)th and so on, and lastly \(s + r\) of the complete primitive system.

\(§ 7.\) The second singular solution of (I.) is the first of (VI.) and (VII.) Now by (VI.) the ratios \(dc_1 : dc_2 : \ldots : dc_n\) are given rationally in terms of \(c_1, c_2, \ldots c_n\), and certain other variables \(x, y_1, \ldots y_s\) which are connected with \(c_1, \ldots c_n\) by the equations (II.) and (VII.). The condition that (II.) and (VII.) shall have two consecutive solutions is
\[
\frac{\partial (F_1, \ldots F_n, \Omega)}{\partial (x, y_1, \ldots y_n)} = 0,
\]
\(\Omega\) being written for the left-hand side of (VII.).

This equation we may write
\[
\left(\frac{\partial}{\partial x} + p_1 \frac{\partial}{\partial y_1} + p_2 \frac{\partial}{\partial y_2} + \ldots\right) \Omega = 0 \quad \text{or} \quad \Delta \Omega = 0,
\]

* Different members of the system are got by giving different sets of values to the arbitrary constants.
where $p_1, p_2, \ldots p_n$ have the values given by the equations (III.), and $c_1, c_2 \ldots$ are treated as constants in the differentiation.

Since $\Omega = 0$, we may use instead of the operator $\Delta$, another, $\nabla$, such that

$$\nabla = \frac{dc_1}{dx} \frac{\partial}{\partial c_1} + \frac{dc_2}{dx} \frac{\partial}{\partial c_2} + \ldots$$

for $\Delta \Omega + \nabla \Omega = 0$.

By comparing $\nabla \Omega = 0$ with (VI.), we see that all the determinants of the matrix

$$\begin{vmatrix}
\frac{\partial \Omega}{\partial c_1} & \frac{\partial F_1}{\partial c_1} & \frac{\partial F_2}{\partial c_1} & \cdots & \frac{\partial F_n}{\partial c_1} \\
\frac{\partial \Omega}{\partial c_2} & \frac{\partial F_1}{\partial c_2} & \frac{\partial F_2}{\partial c_2} & \cdots & \frac{\partial F_n}{\partial c_2} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\frac{\partial \Omega}{\partial c_n} & \frac{\partial F_1}{\partial c_n} & \frac{\partial F_2}{\partial c_n} & \cdots & \frac{\partial F_n}{\partial c_n}
\end{vmatrix}$$

vanish.

§ 8. For the third singular solution we take the further integral equation $\Delta^2 \Omega = 0$ or $\nabla^2 \Omega = 0$, which forms are equivalent, since already $\Omega = 0$, $\Delta \Omega = 0$. The argument is the same as in § 6, and may be carried on till the last singular solution is reached.

The equations $\Omega = 0 = \nabla \Omega = \nabla^2 \Omega = \ldots = \nabla^{r-1} \Omega$, which yield the $r$th singular solution, show that the equations $F_1 = 0 = F_3 = F_3 = \ldots = F_n$, when solved for $c_1, c_2, \ldots c_n$, have $r + 1$ coincident solutions.

§ 9. The equations in the other form, viz., $\Omega = 0$, $\Delta \Omega = 0 \ldots \Delta^{r-1} \Omega = 0$, show that the system

$$F_1 = 0 = F_3 = \ldots = F_n = \Omega$$

is satisfied by $r + 1$ consecutive sets of values of $x, y_1, \ldots y_n$.

For suppose $E$ to be the eliminant of $F_1, F_3, \ldots \Omega$ with respect to $c_1, \ldots c_n$, we have then an identity

$$E = A_1 F_1 + A_2 F_2 + \ldots + A_n F_n + B \Omega.$$ 

Differentiate partially as to $c_1, c_2 \ldots c_n$ in turn, and we have

$$B \frac{\partial \Omega}{\partial c_s} + \sum_{r=1}^n A_r \frac{\partial F_r}{\partial c_s} = - \Omega \frac{\partial B}{\partial c_s} - \sum_{r=1}^n F_r \frac{\partial A_r}{\partial c_s} \quad (s = 1, 2 \ldots n)$$

Eliminating $A_2, \ldots A_n$ on the left-hand side, we find

$$B \frac{\partial (\Omega, F_2, \ldots F_n)}{\partial (c_1, \ldots c_n)} + A_1 \Omega = - \Omega \frac{\partial (B, F_2, \ldots F_n)}{\partial (c_1, \ldots c_n)} - \sum_{r=1}^n F_r \frac{\partial (A_n, F_2, \ldots F_n)}{\partial (c_1, \ldots c_n)}.$$
Now, in general, the coefficient of \( B \) on the left does not vanish when \( \Omega = 0 = F_1 = \ldots = F_s \), and therefore \( B \) must vanish for such values, and must be of the form

\[ C_1F_1 + C_2F_2 + \ldots + C\Omega. \]

Thus with a slight change in the meaning of \( A_1, A_2, \ldots, \)

\[ E = C\Omega^2 + A_1F_1 + \ldots + A_sF_s. \]

Now, \( \Delta F_1 = 0 = \Delta F_2 = \ldots \) identically, and \( \Omega = 0, \Delta\Omega = 0 \ldots \Delta^{r-1}\Omega = 0 \) for systems of values that satisfy one of the \( r \)th system of singular solutions. Hence in such a case

\[ E = 0, \Delta E = 0 \ldots \Delta^rE = 0, \]

and the number of consecutive solutions of the equations

\[ E = 0 = F_1 = F_2 = \ldots = F_s \text{ is } r + 1. \]

**Geometrical Interpretations.** (§§10-13.)

§10. The geometrical application of the above theory to curves in space of \( n + 1 \) dimensions is easy.

The equations (II.) may be taken to represent a series of curves (that is, singly infinite continuous series of points) in such space. Through any point a certain number, \( i, \) of such curves may be drawn, \( i \) being the number of solutions of (II.) when solved for \( c_1, c_2, \ldots c_s. \)

At every point such a curve is met by \( i - 1 \) other curves of the system, and at certain points one of these \( i - 1 \) curves coincides with it.

The direction of the tangent to such a curve is given by the equation (I.) or (III.).

The first singular solution is the envelope of a series of curves of the system, each of which meets the consecutive one, and the locus of all such envelopes is the surface (\( n \)ply infinite series of points) whose equation is \( E = 0 \) (see §4).

In general, the \( r \)th singular solution is the envelope of a series of curves belonging to the \( (r - 1) \)th singular system, and such that each meets the consecutive one; the locus of such envelopes is an \( (n - r + 1) \)ply infinite continuous series of points at each of which \( r + 1 \) consecutive curves of the original system meet, as also do \( r - s + 1 \) of the \( s \)th singular system. All the successive singular curves touch the original curve.

§11. If every curve of the first system (II.) has a node, the equation (VII.) will be satisfied at every point of the node locus, but (VIII.) will not (compare §4). If
every curve has a cusp (VII.) and (VIII.) will be satisfied by the equation to the
cusp locus, but it will not fulfil the condition of being a first integral. If different
curves of the system touch, the tac-locus will satisfy the equation (VIII.) but not
(VII.). All this is exactly parallel to the known theory of single differential equations
of the first order.
§ 12. There is also an application to plane curves.
Suppose that the differential equations (I.) include the following:—

\[ p_1 = y_2, p_2 = y_3 \ldots p_{n-1} = y_n \]

Then the system (I.) simply reduces to an equation of the \( n^{th} \) order and its \( n \) first
integrals make up the system (II.) from which the singular solutions are derived.
If we write the differential equation

\[ f(x, y, p_1, p_2 \ldots p_n) = 0, \]

putting \( y \) for \( y_1 \), then the equation (VIII.) becomes

\[ \frac{\partial f}{\partial p_n} = 0, \]

and this is the first integral (if it is one) from which the singular solutions are
derived.

The final integral, found by eliminating \( p_1, p_2 \ldots p_{n-1} \) from the system (II.), is the
equation to a system of curves, of which there are \( i \) passing through any point and
having at that point contact of the \( (n - 1)^{th} \) order with any assigned curve through
it; all these have contact with one another of the \( (n - 1)^{th} \) order.

If two of them coincide, then a curve of the first singular system passes through
the point and has contact of the \( (n - 1)^{th} \) order with each of the \( i \) curves, and of the
\( n^{th} \) order with either of the two coincident ones.

A curve of the first singular system can be made to have contact of the \( (n - 2)^{th} \)
order with any given curve at any point of it.

At any point of a curve of the second singular system three coincident curves of
the original system and two of the first singular system will satisfy the conditions
for contact with it of the orders \( n - 1, n - 2 \), respectively, and in each case the
contact will be actually of the \( n^{th} \) order, and so in general. The single curve of the
\( n^{th} \) singular system is the envelope of those of the \( (n - 1)^{th} \), but it is more than
an ordinary envelope since its contact with each of the enveloped curves is of the
\( n^{th} \) order.

§ 13. It should be noticed that if \( n - 1 \) of the dependent variables are eliminated
by differentiation from \( n \) simultaneous equations, the new equation, of order \( n \), will be
satisfied by the same complete primitive, but that its singular solutions will generally
be different, since the singular solutions of the system do not furnish the same values as the complete primitive for any but the first differential coefficients (compare § 17 below).

**Singular Solutions Included in the Complete Primitive. (§§ 14–16.)**

§ 14. In certain cases it appears to be possible for the second singular solution to exist without the first.

The ratios \( dc_1 : dc_2 \ldots \) are given by the equations (VI.) and involve \( x, y_1, y_2 \ldots y_n \), which are given in terms of \( c_1, c_2 \ldots \) by the equations (II.) and (VII.). If these are not enough, that is to say, if \( \Omega \) can be expressed in terms of \( c_1, c_2 \ldots c_n \), there is no first singular solution.

For, from \( \Omega = 0 \), may be deduced

\[
\sum_{r=1}^n \frac{\partial \Omega}{\partial c_r} dc_r = 0,
\]

a further linear equation to be satisfied by \( dc_1, dc_2, \ldots \) Thus either \( c_1, c_2 \ldots \) are all constants, or the further integral equation

\[
\frac{\partial}{\partial (c_1, c_2 \ldots c_n)} (F_1, F_2 \ldots F_{n-1}, \Omega) = 0,
\]

whose left-hand side we shall call \( \Omega_1 \), is satisfied.

In virtue of this equation \( \Omega = 0 \) is an integral of the equations (VI.). The values of \( x, y_1 \ldots y_n \) are given in terms of \( c_1, \ldots c_n \) by (II.) and \( \Omega_1 = 0 \), and by substituting these values in (VI.) and finding \( n - 2 \) more integrals of the equations so derived, we get the second singular solution, containing \( n - 2 \) arbitrary constants.

It would, perhaps, be better to say that in such a case the first singular solution is included in the complete primitive, the values of the arbitrary constants being so chosen as to satisfy the equation \( \Omega = 0 \).

If \( \Omega_1 \) can be expressed as a function of \( c_1, \ldots c_n \) only by means of the equations (II.), we must use the equation

\[
\frac{\partial}{\partial (c_1, \ldots c_n)} (F_1, \ldots F_{n-1}, \Omega_1) = 0, \text{ or } \Omega_2 = 0,
\]

to find the third singular solution, the second being included in the first.

Because \( \Omega_2 = 0, \Omega_1 = 0 \) is an integral of (VI.), and because \( \Omega_1 = 0, \Omega = 0 \) is an integral. Therefore \( n - 3 \) integrals are still to be found.

This process may be carried on as far as is needed. It is also to be used if \( \Omega \) has any factor that does not involve \( x, y_1 \ldots y_n \).

* It sometimes happens that the equations (I.) and (VII.) are enough to define \( x, y_1 \ldots y_n \) in terms
§ 15. The case of § 14 presents itself quite naturally if we start from the differential equations (I.) instead of from the integrals (II.). Let \( \phi \), as before, be a factor of \( E \).

There is no apparent reason why the equation

\[
\frac{d\phi}{dx} = 0
\]

should follow algebraically from the system (I.) and the equation \( \phi = 0 \).

Let \( E_1 = 0 \) be the result of eliminating \( p_1, p_2 \ldots p_n \) from the system (I.) and the equation \( d\phi_1/dx = 0 \).

Let \( \phi_1 \) be a factor of \( E_1 \) and let \( E_2 = 0 \) be the result of eliminating \( p_1, \ldots p_n \) from the system (I.) and \( d\phi_2/dx = 0 \), and so on for \( \phi_2, \phi_3 \ldots \)

There is no apparent reason why any function in the series \( \phi, \phi_1, \phi_2 \ldots \) should vanish because all those before it are supposed to vanish. If one of them, say \( \phi_r \), does satisfy this condition, then the equations

\[
\phi = 0 = \phi_1 = \phi_2 = \ldots = \phi_{r-1}
\]

are integrals of (I.), and by using them and finding \( n-r \) other integrals, each containing an arbitrary constant, we have a singular solution of the \( r \)th system.

§ 16. Thus, as in the simpler case when there is a single equation of the first order, the existence of singular solutions appears to be the rule if we consider the integrals, the exception if we consider the differential equations, and in fact the number of conditions for the absence of the first \( r \) singular solutions rises with \( r \) from the first point of view, while the generality of the conditions for the existence of the \( (r+1) \)th from the second point of view decreases as \( r \) increases.

of \( c_1, c_2 \ldots c_n \), but that when \( x, y_1 \ldots y_n \) are eliminated from (VI.) by this means, an integral equation presents itself as an alternative to a differential equation. In such a case the integral equation will, of course, relate to the second singular solution, for it contains no arbitrary constant.

Considered geometrically, the second singular solution thus arising will be enveloped by the complete primitive, and, therefore, also by the first singular solution (for both lie on the locus of singular solutions \( E = 0 \)), although it may not be a singular solution of the differential equations (VI.).

A proper change in the forms of the arbitrary constants would reduce this case to the ordinary one. If the integral factor is \( \sigma^{c_1} \phi^{c_2} \ldots \), \( \phi \ldots \) being functions of \( c_1, c_2 \ldots \) then if in the system of arbitrary constants we take \( \sigma \phi \ldots \) instead of \( c_1 \), the factor will disappear.

In fact the ordinary equation

\[
y = px - p^3,
\]

or any other, may be transformed so that its singular solution appears as an integral factor. Put

\[
y = \frac{1}{4} (x^2 - z^2)
\]

and we find

\[
y - px + p^2 = \frac{1}{4} z^2 (z^2 - 1).
\]
Examples. I. Congruency of Bitangents to a Torse. (§§ 17-19.)

§ 17. The simplest examples are equations of Clairaut's form, such as

\[
\begin{align*}
  y_1 &= p_1 x + p_1^2 + p_1 p_2 + p_2, \\
  y_2 &= p_2 x + p_1 p_2 + p_2^2
\end{align*}
\]

The complete primitive is

\[
\begin{align*}
  y_1 &= c_1 x + c_1^2 + c_1 c_2 + c_2, \\
  y_2 &= c_2 x + c_1 c_2 + c_2^2
\end{align*}
\]

The singular solutions are given by the equations

\[
\begin{align*}
  0 &= (x + 2c_1 + c_2) \, dc_1 + (c_1 + 1) \, dc_2, \\
  0 &= c_2 \, dc_1 + (x + c_1 + 2c_2) \, dc_2
\end{align*}
\]

Hence, by eliminating \( x \),

\[
(c_2 \, dc_1 - c_1 \, dc_2) \, (dc_1 + dc_2) = dc_2^2
\]

This is also of Clairaut's form, and its integral is

\[
(1 - \mu) \, c_2 - \mu c_1 = \mu^2
\]

so that

\[ dc_2 : dc_1 : : \mu : 1 - \mu. \]

Thus

\[
\begin{align*}
  (x + 2c_1 + c_2) \, (1 - \mu) + \mu \, (c_1 + 1) &= 0, \\
  2c_1 &= - \mu^2 - \mu - x + \mu x, \\
  2c_2 &= \mu^2 - \mu x, \\
  4y_1 &= (\mu - x) \, (\mu^2 + 3\mu + x - x\mu), \\
  4y_2 &= - \mu \, (\mu - x)^2
\end{align*}
\]

The equations (\( \xi \)) furnish the first singular solution. For the second we must make (\( \varepsilon \)), as a quadratic in \( \mu \), have equal roots, that is, we must put

\[
\begin{align*}
  2\mu &= - c_1 - c_2, \\
  2c_2 &= \mu \, (c_1 + c_2).
\end{align*}
\]
OF SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS.

From these and the former equations we find

\[ \mu = \frac{1}{3}x, \quad c_1 = \frac{1}{3}x^2 - \frac{2}{3}x, \quad c_2 = -\frac{1}{9}x^2. \]

\[ \begin{aligned}
    y_1 &= \frac{1}{37}x^3 - \frac{1}{3}x^2, \\
    y_2 &= -\frac{1}{37}x^3
\end{aligned} \]  \hspace{0.5cm} (\eta).

The equations (\eta) are the second singular solution.

We have here an example of what was pointed out in § 13. If we differentiate the equations (\alpha) and eliminate \( y_2 \) and \( p_2 \), the resulting differential equation of the second order is

\[ \frac{d^2 y_1}{dx^2} = 0. \]

This is satisfied by the complete primitive (\beta), but not by either of the singular solutions.

§ 18. To find the singular solutions from the original equations, we have first to try if the equation

\[ \begin{vmatrix}
    x + 2p_1 + p_2, & p_1 + 1 \\
    p_2, & x + 2p_2 + p_1
\end{vmatrix} = 0 \]  \hspace{0.5cm} (\theta)

can be used as a first integral.

The elimination of \( p_1 \) and \( p_2 \) gives

\[ 4(y_1 + y_2)^3 + x^2(y_1 + y_2)^3 + 4x^3y_2 + 18xy_2(y_1 + y_2) - 27y_2^2 = 0. \]  \hspace{0.5cm} (i)

It is easily verified that the derivative of this equation is an algebraical consequence of it in virtue of the original differential equations.

§ 19. If we take \( x, y_1, y_2 \) as Cartesian co-ordinates, the equations (\beta) represent a line common to two osculating planes of the twisted cubic (\eta), (\xi) represent the conic enveloped by this line when one of the osculating planes is fixed and the other variable, and (i) is the equation to the torse enveloped by the osculating planes.

The General Case. (§§ 20, 21.)

§ 20. For any other twisted curve there is a similar theory.

Let

\[ x + Ay_1 + By_2 + C = 0 \]

be the equation to an osculating plane, \( A, B, C \) being functions of a parameter \( \mu \).

Let \( A, B, C \) denote the same functions of \( \mu \), and let \( A, B, C \) be written for \( dA/d\mu, dB/d\mu, dC/d\mu, \).
Then by eliminating $\mu_1$ and $\mu_2$ from the four equations
\begin{align*}
1 + A_1 p_1 + B_1 p_2 &= 0, \quad x + A_1 y_1 + B_1 y_2 + C_1 = 0, \\
1 + A_2 p_1 + B_2 p_2 &= 0, \quad x + A_2 y_1 + B_2 y_2 + C_2 = 0,
\end{align*}
we have two relations which may be put in the Clairaut form
\begin{align*}
y_1 &= p_1^2 x + \phi_1 (p_1, p_2), \\
y_2 &= p_2^2 x + \phi_2 (p_1, p_2).
\end{align*}

§ 21. The complete primitive of these equations will represent the trace of any one osculating plane on any other. The singular solutions are given by
\begin{align*}
(A' y_1 + B' y_2 + C'_1) \frac{d\mu_1}{dx} &= 0, \\
(A'_2 y_1 + B'_2 y_2 + C'_2) \frac{d\mu_2}{dx} &= 0.
\end{align*}

For the first singular solution, either $\mu_1$ or $\mu_2$ is to be equated to a constant, while the other satisfies the equation
\[ A'y_1 + B'y_2 + C' = 0. \]
The first singular solution is, therefore, the trace on any osculating plane of the torse which they all envelope.

For the second we must suppose both $\mu_1$ and $\mu_2$ to satisfy the equation
\[ A'y_1 + B'y_2 + C' = 0. \]

This gives the original curve, which is the cuspidal edge of the torse, together with the nodal curve of the torse. The latter is not a solution of the differential equations.

**Example II. A Bitangential Congruency. (§§ 22-26.)**

§ 22. Take for another example the equations
\begin{align*}
(A + B p_1^2 + C p_2^2) \{B (y_1 - p_1 x)^2 + C (y_2 - p_2 x)^2 - 1\} &= \{B p_1 (y_1 - p_1 x) + C p_2 (y_2 - p_2 x)\}^2, \\
(a + b p_1^2 + c p_2^2) \{b (y_1 - p_1 x)^2 + c (y_2 - p_2 x)^2 - 1\} &= \{b p_1 (y_1 - p_1 x) + c p_2 (y_2 - p_2 x)\}^2.
\end{align*}

These define $y_1 - p_1 x$, and $y_2 - p_2 x$ as functions of $p_1$ and $p_2$, and are, therefore, of the Clairaut form, and may be integrated by substituting $c_1$ for $p_1$ and $c_2$ for $p_2$.

The integral in this form will represent four lines of a congruency, which consists in fact of all the common tangents to the two quadric surfaces.
The first of the differential equations may be written
\[(A + Bp_1^2 + Cq_2^2) (Ax^2 + By_1^2 + Cy_2^2 - 1) = (Ax + By_1p_1 + Cy_2q_2)^2.\]

One of the integrals is, therefore,
\[(A + Bc_1^2 + Cc_2^2) (Ax^2 + By_1^2 + Cy_2^2 - 1) = (Ax + By_1c_1 + Cy_2c_2)^2.\]

Thus, one of the equations that give the singular solutions is
\[(Bc_1 dc_1 + Cc_2 dc_2) (Ax^2 + By_1^2 + Cy_2^2 - 1) = (By_1 dc_1 + Cy_2 dc_2) (Ax + By_1c_1 + Cy_2c_2).\]

Unless
\[Ax^2 + By_1^2 + Cy_2^2 - 1 = 0 \quad \text{and} \quad Ax + By_1c_1 + Cy_2c_2 = 0,
\]
this may be reduced to
\[(Bc_1 dc_1 + Cc_2 dc_2) (Ax + By_1c_1 + Cy_2c_2) = (By_1 dc_1 + Cy_2 dc_2) (A + Bc_1^2 + Cc_2^2).\]

This last equation only contains \(x, y_1, y_2\), in the combinations \(y_1 - c_1x, y_2 - c_2x\), and the same will be true for the other equation of the same form that may be derived from the second equation of the complete primitive.

From these two equations and those of the complete primitive we can eliminate the ratio \(dc_1 : dc_2\), and the expressions \(y_1 - c_1x\) and \(y_2 - c_2x\), so as to have an equation in \(c_1\) and \(c_2\) only. In accordance with § 14 the first singular solution thus given will be included in the complete primitive, and the only proper first singular solutions are given by taking
\[ax^2 + by_1^2 + cy_2^2 - 1 = 0 \quad \text{and} \quad ax + by_1c_1 + cy_2c_2 = 0,
\]
or
\[Ax^2 + By_1^2 + Cy_2^2 - 1 = 0 \quad \text{and} \quad Ax + By_1c_1 + Cy_2c_2 = 0.
\]

§ 23. In order to integrate for the first singular solution, it will be useful to transform the equations to others in terms of \(t, u, v\), the values of \(\mu\) which satisfy the equation
\[\frac{Ax^2}{a + \mu A} + \frac{By_1^2}{b + \mu B} + \frac{Cy_2^2}{c + \mu C} - \frac{1}{1 + \mu} = 0.
\]
The differential equations are then reduced to
\[
\Sigma \frac{(dt)^2}{(u - v) (1 + t) (a + tA) (b + tB) (c + tC)} = 0,
\]
and
\[
\Sigma \frac{(dt)^2}{(u - v) (1 + t) (a + tA) (b + tB) (c + tC)} = 0.
\]

If \(Ax^2 + By_1^2 + C_2^2 - 1 = 0\), then \(t, u, v\), or \(v\) vanishes, say \(t\); the first equation is satisfied, and the second is reduced to
\[
\frac{u (da)^2}{(1 + u) (a + uA) (b + uB) (c + uC)} = \frac{v (dc)^2}{v (1 + v) (a + vA) (b + vB) (c + vC)}.
\]

The variables are here separated, so that we have one first singular solution. The other is given by taking
\[
ax^2 + by_1^2 + cy_2^2 - 1 = 0,
\]
and
\[
\frac{(da)^2}{u (1 + u) (a + uA) (b + uB) (c + uC)} = \frac{(dc)^2}{v (1 + v) (a + vA) (b + vB) (c + vC)}.
\]

Either of these two solutions gives as the second singular solution
\[
\begin{cases}
ax^2 + by_1^2 + cy_2^2 - 1 = 0, \\
Ax^2 + By_1^2 + C_2^2 - 1 = 0.
\end{cases}
\]

* In carrying out the reduction we may use the formula
\[
\frac{Aax^2 + Bby_2^2 + C_2^2 - 1}{a + \mu A + b + \mu B + c + \mu C} = \frac{(a - A) (b - B) (c - C) (u - t) (u - v) (u - v)}{(a + \mu A) (b + \mu B) (c + \mu C)}.
\]

and differentiate it, considering \(\mu\) as constant and \(t, u, v, y_1, y_2\) as functions of \(x\).

The expression
\[
\frac{Aax}{a + \mu A} (dx)^2 + \frac{Bb}{b + \mu B} (dy_1)^2 + \frac{Cc}{c + \mu C} (dy_2)^2
\]
may then be expressed in terms of \(dt, du, dc\) by means of the formulæ for \(x, y_1, y_2\), in terms of \(t, u, v\).

It will thus be found that the equation
\[
\left(\frac{Aax}{a + \mu A} + \frac{Bby_1}{b + \mu B} + \frac{C_2^2}{c + \mu C}\right)^2 = \left(\frac{Aax}{a + \mu A} + \frac{Bby_1}{b + \mu B} + \frac{C_2^2}{c + \mu C} - \frac{1}{1 + \mu}\right)
\]
\[
\times \left(\frac{Aax}{a + \mu A} + \frac{Bby_1}{b + \mu B} + \frac{C_2^2}{c + \mu C}\right)
\]
reduces to
\[
\Sigma \frac{dc}{(u - v) (1 - \mu) (1 + t) (a + \mu A) (b + B) (c + Ct)} = 0.
\]
§ 24. In order to find the other second singular solution let us write $T$, $U$, $V$ for $(u - v) (1 + t) (a + tA) (b + tB) (c + tC)$, and the two symmetrical expressions.

The differential equations, cleared of fractions, may then be written

$$UVuv + VTuv \left( \frac{du}{dt} \right)^2 + TUtuv \left( \frac{dv}{dt} \right)^2 = 0,$$

$$UV + VT \left( \frac{du}{dt} \right)^2 + TU \left( \frac{dv}{dt} \right)^2 = 0.$$

The Jacobian of these expressions with respect to $du/dt$ and $dv/dt$ is

$$4 \frac{du}{dt} \frac{dv}{dt} TUV (v - u),$$

the square of which reduces to a constant multiple of

$$TUV^3uv (t - u)(t - v).$$

The factors of this expression are to be considered in turn.

Now the vanishing of such a factor as $1 + t$ or $a + At$ only causes two solutions of the equations giving $x$, $y_1$, $y_2$ in terms of $t$, $u$, $v$ to coincide and only yields a solution of the transformed, not of the original, equations.

The solutions given by supposing $t$, $u$ or $v$ to vanish or be infinite have been considered. The case when two of the three are equal is left.

If $t = u$, then $V = 0$, so that the equations give

$$TU (dv/dt)^2 = 0.$$

Suppose first that $v$ is constant.

It is easily found, as in the theory of confocal conicoids, that

$$x^2 = \frac{(b - B)(c - C)}{AA(aB - Ab)} \frac{(a + At)(a + An)(a + Av)}{(1 + t)(1 + u)(1 + v)}$$

with like values for $y_1^2$ and $y_2^2$.

Thus if $t = u$ and $v$ is constant, $x$, $y_1$, $y_2$ are constant multiples of

$$\frac{a + At}{1 + t}, \frac{b + B}{1 + t}, \frac{c + Ct}{1 + t}.$$

Hence $y_1$ and $y_2$ are linear functions of $x$ and $p_1$, $p_2$ are constants connected by a single relation since they involve the arbitrary constant $v$. This solution is therefore included in the complete primitive and must be the same as was rejected in § 22.
§ 25. If \( t = u \) and \( v \) is not constant, then \( TU = 0 \) and \( v = t \), or else \((1 + t)(a + At)(b + Bt)(c + Ct) = 0\).

The latter condition leads to no solution.

For the second singular solution we must take \( t = u = v \), whence we find that each determinant of the matrix

\[
\begin{vmatrix}
ax^5, & \beta y_1^5, & \gamma y_2^5, & 1 \\
\alpha, & \beta, & \gamma, & 1 \\
A, & B, & C, & 1
\end{vmatrix}
\]

if \( a, \beta, \gamma \) are the cube roots of

\[
\frac{Aa(aB - Ab)}{(b - B)(c - C)}, \text{ &c.}
\]

§ 26. In the geometrical interpretation it will fix the ideas if we suppose the two conicoids projected into confocals.

The complete primitive represents their common tangents. The first singular solution gives the geodesics on each that touch the other, and the second includes the curve of intersection, which is the envelope of these geodesics.

The common tangent planes envelope a torse, whose generators will be common tangent lines. Of the four common tangents to the surfaces from any point of the torse, two will coincide with the generator of the torse. The equation to this torse is \( t = u \), and every generator of it is a generator of one confocal of the system. Thus the equations \( t = u, v = \text{const} \) represent the different generators of this torse, and their occurrence as an apparent singular solution is accounted for.

The cuspidal edge of this torse is a second singular solution, and is represented by the equations

\[
\begin{vmatrix}
ax^5, & \beta y_1^5, & \gamma y_2^5, & 1 \\
\alpha, & \beta, & \gamma, & 1 \\
A, & B, & C, & 1
\end{vmatrix} = 0.
\]

The General Case. (§§ 27–38.)

§ 27. The straight lines

\[
y_1 = c_1x + b_1 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (1),
\]

\[
y_2 = c_2x + b_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (2),
\]

where the quantities \( b_1, b_2, c_1, c_2 \) are connected by two relations, but are otherwise arbitrary, form a congruency, and, if the relations are properly chosen, may be made to represent any congruency.
Thus the lines of any congruency satisfy differential equations of Clairaut's form.

§ 28. If two consecutive lines meet, the equations (1) and (2), with

\[ 0 = xdc_1 + db_1 \]  
\[ 0 = xdc_2 + db_2 \]

must form a consistent system.

Hence

\[ db_1 dc_2 - db_2 dc_1 = 0 \]

This equation gives two values for the ratio \( dc_1 : dc_2 \), and shows, therefore, that each line of the system meets two consecutive lines (Salmon, "Geometry of Three Dimensions," § 456).

We are supposing that \( b_1, b_2 \) are regarded as functions of \( c_1, c_2 \).

§ 29. The elimination of \( c_1, c_2, dc_1, dc_2 \) from the equations (1), (2), (3), (4) will give the equation to a surface, and the tangent plane to this surface will contain the line (1), (2). For the equation to the tangent plane is found by eliminating \( dc_1, dc_2, dx \) from the differentials of (1) and (2) and of

\[ x + \frac{\partial b_1}{\partial c_1} + \lambda \frac{\partial b_2}{\partial c_1} = 0 \]

\[ \frac{\partial b_1}{\partial c_2} + \lambda \left( x + \frac{\partial b_2}{\partial c_2} \right) = 0 \]

and substituting \( X = x, Y_1 = y_1, Y_2 = y_2 \) for \( dx, dy_1, dy_2 \) (6) and (7) are found from (3) and (4) by the use of the undetermined multiplier \( \lambda \).

From (1) and (2) we have, considering \( c_1 \) and \( c_2 \) and therefore also \( b_1 \) and \( b_2 \) as functions of \( x, y_1, y_2, \)

\[ dy_1 = c_1 dx + x dc_1 + db_1, \]
\[ dy_2 = c_2 dx + x dc_2 + db_2, \]

and therefore in virtue of (6) and (7)

\[ dy_1 + \lambda dy_2 = (c_1 + \lambda c_2) dx. \]

The equation to the tangent plane is therefore

\[ Y_1 - c_1 X + \lambda (Y_2 - c_2 X) = y_1 - c_1 x + \lambda (y_2 - c_2 x) \]

\[ = b_1 + \lambda b_2, \]

and the tangent plane contains the line (1), (2).
§ 30. Hence if the equation (5) gives unequal values for $dc_1 : dc_2$, the lines of the congruency are bitangents to the surface whose equation is found by eliminating $c_1$, $c_2$, $\lambda$ from (1), (2), (6), (7).

The singular solutions of the differential equations are the solutions of (5), that is, of

$$\frac{\partial b_1}{\partial c_1} dc_1 \cdot dc_2 + \left( \frac{\partial b_1}{\partial c_1} - \frac{\partial b_2}{\partial c_2} \right) dc_1 \cdot dc_2 - \frac{\partial b_2}{\partial c_1} dc_1 = 0,$$

an ordinary differential equation connecting $c_1$ and $c_2$, from the solution of which two equations are to be found free from $c_1$ and $c_2$ by help of (1), (2), (6), and (7).

§ 31. The equation connecting $\lambda$, $c_1$, $c_2$ is

$$\lambda^2 \frac{\partial b_2}{\partial c_1} + \lambda \left( \frac{\partial b_1}{\partial c_1} - \frac{\partial b_2}{\partial c_2} \right) - \frac{\partial b_1}{\partial c_2} = 0.$$

Now

$$dy_1 = c_1 \, dx + x \, dc_1 + db_1$$

$$= c_1 \, dx - \lambda \frac{\partial b_2}{\partial c_2} \, dc_1 + \frac{\partial b_1}{\partial c_2} \, dc_2 \text{ by (6)},$$

$$dy_2 = c_2 \, dx + \frac{\partial b_2}{\partial c_1} \, dc_1 - \frac{1}{\lambda} \frac{\partial b_1}{\partial c_2} \, dc_2 \text{ by (7)}.$$

But if the differential equation is to be satisfied we must have

$$dy_1 = c_1 \, dx, \quad dy_2 = c_2 \, dx,$$

and therefore

$$dc_1 + \mu \, dc_2 = 0,$$

where

$$\lambda \mu \frac{\partial b_2}{\partial c_1} = - \frac{\partial b_1}{\partial c_2},$$

so that $\mu$ is the second root of the quadratic for $\lambda$. This can only hold at one point of contact.

§ 32. The integral of the equation (5) thus represents a double system of curves on the surface, one curve being traced by each point of contact of the double tangent. One curve is such that every tangent to it touches the surface again. This is the first singular solution. The other curve is the locus of the other points of contact of the tangents to the first and is not a solution.* One curve of each system goes

* In the case of § 17, this curve is found to be the straight line

$$y_1 = x (\mu^2 - 2\mu) + 3\mu^2 - 2\mu^2,$$

$$y_2 = -x \mu^2 + 2\mu^3,$$

and it is included in the complete primitive.

This will always happen if the surface is developable, for the first singular solution is then the section of
through each point of the surface for every double tangent that can be drawn to touch the surface there.

§ 33. As to the second singular solution, it is apparently given by the equation
\[ \lambda = \mu \text{ (these are the two values given for } - \frac{dc_1}{dc_2}, \text{ or) } \]
\[ \left( \frac{\partial b_1}{\partial c_1} - \frac{\partial b_2}{\partial c_2} \right)^2 + 4 \frac{\partial b_1}{\partial c_2} \cdot \frac{\partial b_2}{\partial c_1} = 0. \]

If there is such a solution, which is not generally to be expected, it will represent a curve on the surface every tangent to which meets the surface in four consecutive points. Such tangents to the surface do not, however, generally envelope a curve on it.

Case of a Nodal Curve. (§ 34.)

§ 34. The case of a surface having a nodal curve deserves consideration.

The tangent to such a curve meets the surface in four consecutive points, and is therefore to be counted as a bitangent. The curve satisfies the same differential equations as the bitangents, and the two values of \( \lambda \) given by the elimination of the differentials from (3) and (4) are equal, so that the curve is to be reckoned as derived from the singular solution of (5), or as a second singular solution of (1) and (2).

But here a paradox presents itself. There are two tangent planes, and therefore two values of \( \lambda \), whereas the equations (6) and (7) only yield one unless they are identities.

We have then
\[ x = - \frac{\partial b_1}{\partial c_1} = - \frac{\partial b_2}{\partial c_2}, \]
\[ \frac{\partial b_1}{\partial c_1} = \frac{\partial b_2}{\partial c_2} = 0. \]

Generally, these equations are not consistent, and therefore, generally, there will be no nodal curve.

But on the other hand it will generally be possible to find a singly infinite series of values of \( x, y_1, y_2 \), such that the equations (1) and (2), solved for \( b_1, b_2, c_1, c_2 \), shall have two pairs of coincident solutions, and the corresponding curve will be a nodal curve on the surface.

The explanation of the paradox is that the surface will generally have other bitangents as well as those belonging to the given congruency. These will form the surface by a variable tangent plane and the tangent to this section touches the surface again at a point on the generator along which the plane touches the surface. The generator is therefore the locus of the second point of contact, and as it is the intersection of consecutive tangent planes it is included in the complete primitive.
another congruency, satisfying another pair of differential equations, which the nodal curve also satisfies.

For instance, the normals to an ellipsoid are bitangents to the surface of centres, but there are other bitangents, which form three more congruencies (see Salmon, ‘Geometry of Three Dimensions,’ § 511a). The double curve satisfies the differential equations to the congruency of “synnormals.”

If we reciprocate we find the same paradox in relation to the double tangent planes. The line joining the points of contact will generally belong to the second congruency, and the cuspidal edge of the torse which it generates will satisfy the differential equations to this congruency, and belong to its second singular solution, the corresponding first being included in the complete primitive.

Case of a Cuspidal or Parabolic Curve. (§ 35.)

§ 35. At first sight it would appear as if a cuspidal curve ought to satisfy the differential equations to the bitangents, since any tangent to it meets the surface in four consecutive points. But the consideration of the reciprocal surface shows that the tangent planes drawn through such a tangent include three coincident ones, not two distinct coincident pairs. The tangents to a cuspidal curve and the inflexional tangents at parabolic points are therefore not to be counted as bitangents.

When a surface is varied continuously so that a nodal curve changes into a cuspidal, some of the bitangents become chords of the cuspidal curve, and among them are to be reckoned the tangents to that curve. In the same way the inflexional tangents at parabolic points are included in the congruency formed by the intersections of tangent planes at pairs of parabolic points. Thus in a sense the congruency of chords of the cuspidal curve, and that of double tangents to the torse enveloped by the tangent planes at parabolic points, are limiting forms of bitangential congruencies belonging to the surface, though they cannot be considered as true bitangential congruencies belonging to it.

Digression on a Certain Singularity of Surfaces. (§§ 36, 37.)

§ 36. If, however, the curve is both cuspidal and inflexional, in a sense which we shall shortly explain, the tangents to it are true bitangents to the surface.

If we suppose the inflexional tangent at each parabolic point to coincide with the tangent to the parabolic curve, then that curve must be plane or else a double curve on the surface. For the tangent plane at each parabolic point coincides with that at the consecutive point along the inflexional tangent, and hence the tangent plane is the same all along the parabolic curve. A double curve will, however, satisfy the conditions, if we consider the tangent plane at each point as indeterminate. But a nodal
curve will be an irrelevant solution, unless it has the singularity in question on one or other of the two sheets. A cuspidal curve may yield us the true solution.

Now it is easily proved that the osculating plane of a curve traced on a surface will coincide with the tangent plane to the surface when it touches one of the inflexional tangents, and only then. The osculating planes of the curve we are discussing will, therefore, be the tangent planes to the surface at the points where they osculate the curve.

Thus the singularity under discussion consists of a cuspidal curve, such that the osculating plane at every point of it touches the surface at that point. The corresponding singularity on the reciprocal surface is of the same kind.

§ 37. To prove this write the equation to the surface (multiplied by a factor, it may be) in the form \( \lambda \phi^2 = \mu \psi^3 \), \( \lambda, \mu, \phi, \psi \) being functions of \( x, y, z \), such that \( \phi = \psi = 0 \) are the equations to the cuspidal curve.

Put

\[ \phi = \mu \psi = t, \]
then

\[ \psi = \ell^3 \mu, \quad \phi = \ell^3 \mu^2. \]

Suppose now that

\[ \phi = \phi_2 + \phi_3 + \ldots \]
\[ \psi = \psi_2 + \psi_3 + \ldots \]

\( \phi_2 \) and \( \psi_2 \) being homogeneous in \( z, y, x \) and of the degree \( r \).

Then we may deduce expansions for \( y \) and \( z \) in ascending powers of \( t \) and \( x \) as follows—

\[ y = \alpha t^3 + \beta t^3 + \ldots \]
\[ + x (\gamma t^3 + \ldots) \]
\[ + x^2 (\delta + \epsilon t^3 + \ldots) \ldots \]
\[ z = \alpha' t^3 + \beta' t^4 + \ldots \]
\[ + x (\gamma' t^3 + \ldots) \]
\[ + x^2 (\delta' + \epsilon' t^3 + \ldots) + x^3 (\ell' + \ldots), \]

the first power of \( t \) being absent throughout.

More generally, we have in the neighbourhood of a cuspidal curve \( (t = 0) \) expansions of the form

\[ x = x_0 + tx_1 + t^2 x_2 + \ldots \]
\[ y = y_0 + ty_1 + t^2 y_2 + \ldots \]
\[ z = z_0 + tz_1 + t^2 z_2 + \ldots \]
\[ w = w_0 + tw_1 + t^2 w_2 + \ldots \]
where \(x_0, y_0 \ldots x_1, y_1 \ldots\) are functions of a second variable \(u\), such that all the determinants of the matrix
\[
\begin{vmatrix}
  x_1, & y_1, & z_1, & w_1 \\
  x_0, & y_0, & z_0, & w_0 \\
  x_0', & y_0', & z_0', & w_0'
\end{vmatrix}
\]
vanish, dashes being used to indicate differentiation with respect to \(u\), and dots differentiation with respect to \(t\).

If \(\xi, \eta, \zeta, \omega\) are the determinants of the matrix
\[
\begin{vmatrix}
  x, & y, & z, & w \\
  x', & y', & z', & w' \\
  x', & y', & z', & w'
\end{vmatrix}
\]
then the reciprocal surface is the locus of \((\xi, \eta, \zeta, \omega)\).

We will now find whether the curve \(t = 0\) on the reciprocal surface can be cuspidal.

If \(\xi, \eta, \zeta, \omega\) are expanded in powers of \(t\) we have at once \(\xi_0 = 0, \eta_0 = 0, \zeta_0 = 0, \omega_0 = 0\), \(\xi\), \(\eta\), \(\zeta\) denoting the coefficient of \(t^n\) in \(\xi\), and so on.

We also find
\[
\begin{align*}
x_0 \xi_1 + y_0 \eta_1 + z_0 \zeta_1 + w_0 \omega_1 &= 0, \\
x_0 \xi_2 + y_0 \eta_2 + z_0 \zeta_2 + w_0 \omega_2 &= 0, \\
x_0' \xi_1 + y_0' \eta_1 + z_0' \zeta_1 + w_0' \omega_1 &= 0, \\
x_0' \xi_2 + y_0' \eta_2 + z_0' \zeta_2 + w_0' \omega_2 &= 2.
\end{align*}
\]
and hence, differentiating the first and using the third,
\[
x_0 \xi_1' + y_0 \eta_1' + z_0 \zeta_1' + w_0 \omega_1' = 0.
\]
Also
\[
\begin{align*}
x_0'' \xi_1 + y_0'' \eta_1 + z_0'' \zeta_1 + w_0'' \omega_1 &= 2, \\
x_0'' \xi_2 + y_0'' \eta_2 + z_0'' \zeta_2 + w_0'' \omega_2 &= -2, \\
\end{align*}
\]
so that
\[
x_0' \xi_1' + y_0' \eta_1' + z_0' \zeta_1' + w_0' \omega_1' = 2\Delta.
\]
OF SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS.

If \( \lambda, \mu \) are quantities such that
\[
x_1 = \lambda x_0 + \mu x_0', \quad y_1 = \lambda y_0 + \mu y_0', \text{ etc.,}
\]
then it is clear that \( \Delta_1 = \mu \Delta \).

Hence, if \( \Delta = 0 \), all the determinants of the matrix
\[
\begin{vmatrix}
\xi_1, & \eta_1, & \xi_1, & \omega_1 \\
\xi_2, & \eta_2, & \xi_2, & \omega_2 \\
\xi_1', & \eta_1', & \xi_1', & \omega_1'
\end{vmatrix}
\]
vanish.

This is the condition that the curve \( t = 0 \) should be cuspidal on the reciprocal surface, for the common factor \( t \) has to be taken out of the expressions for \( \xi, \eta, \zeta, \omega \), and the expressions for the coordinates become
\[
\frac{\xi}{t} = \xi_1 + \xi_2 + \ldots \text{ etc.}
\]

We find, moreover, that
\[
x_0 \xi_3 + y_0 \eta_3 + z_0 \zeta_3 + w_0 \omega_3 = -\mu^3 \Delta = 0,
\]
so that the reciprocal surface satisfies the condition
\[
\begin{vmatrix}
\xi_3, & \eta_3, & \zeta_3, & \omega_3 \\
\xi_1, & \eta_1, & \zeta_1, & \omega_1 \\
\xi_1', & \eta_1', & \zeta_1', & \omega_1' \\
\xi_1'', & \eta_1'', & \zeta_1'', & \omega_1''
\end{vmatrix} = 0,
\]
which is of the same form as \( \Delta = 0 \).

Hence this singularity is of the same kind as its reciprocal. The tangents to a curve of this kind are true bitangents to the surface, since they meet it in four consecutive points, and their reciprocals meet the reciprocal surface in four consecutive points.

Lastly the condition \( \Delta = 0 \) is that which must be satisfied if the tangent plane to the surface, namely
\[
\begin{vmatrix}
x, & y, & z, & w \\
x_0, & y_0, & z_0, & w_0 \\
x_0', & y_0', & z_0', & w_0' \\
x_2, & y_2, & z_2, & w_2
\end{vmatrix} = 0,
\]
coincides with the osculating plane of the cuspidal curve, that is
\[
4 \Delta 2
\]
This proves the theorem.

It is clear that the cuspidal edges of developable surfaces belong to this category, and thus the second singular solution in Example I. is accounted for.

Example III. (§ 38.)

§ 38. As an example, we will take the system of lines represented by the differential equations

$$y_1 = p_1 x + rac{1}{2} p_2^3,$$
$$y_2 = p_2 x + rac{1}{2} p_1^2.$$

It will be more convenient to use $y, z, p, q$ instead of $y_1, y_2, p_1, p_2$. The complete primitive is clearly

$$y = \mu x + \frac{1}{3} \nu^3,$$
$$z = \nu x + \frac{1}{2} \mu^2.$$

The singular solutions are given by the system

$$x \frac{d\mu}{x} + \nu^3 \frac{dv}{x} = 0,$$
$$x \frac{dv}{x} + \mu \frac{d\mu}{x} = 0.$$

We find

$$x = \mu^3 \nu,$$
$$\nu \frac{d\mu}{nu} + \nu \frac{dv}{nu} = 0,$$
$$\frac{3}{2} \mu^3 + \frac{1}{2} \nu^3 = c, \text{ a constant.}$$

Thus, for the first singular solution,

$$x^3 = \frac{3}{4} \nu^3 (2c - \nu^3),$$
$$y = \mu x + \frac{1}{3} \nu^3$$
$$= \frac{1}{3} \nu (18c - 5\nu^3),$$
$$z = \nu x + \frac{1}{2} \mu^2 = \frac{3}{8} \nu (6c + 5\nu^3).$$

By eliminating $\nu$ from these equations we have the two equations to a curve belonging to the first singular solution, that is to an envelope of the bitangents.
OF SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS.

If now we take the other value of \( x \) given by the quadratic \( x^2 = \mu \nu^2 \) we find for the other point of contact

\[
x^3 = -\frac{8}{3} \nu^3 (2c - \nu^2),
\]
\[
y = -\frac{1}{3} \nu (18c - 13\nu^2),
\]
\[
z = -\frac{x}{8\nu} (6c - 11\nu^2).
\]

The elimination of \( \nu \) from these equations gives the locus of the other point of contact.

There is no second singular solution.

The equation to the surface which has the lines for bitangents is to be found by eliminating \( \mu, \nu \) from

\[
x^2 = \mu \nu^3
\]
\[
y = \mu x + \frac{1}{3} \nu^3
\]
\[
z = \nu x + \frac{1}{3} \mu \nu^3.
\]

It is

\[
3125x^{12} - 9000x^5y^2 + 8100x^3y^2z + 2592x^2yz^3 - 1944x^3y^5 - 2592x^2y^3z^4 + 648y^4z^3 = 0.
\]

Any point of this surface may be represented by the coordinates

\[
\left( \xi, \frac{\xi^3}{\nu^2} + \frac{1}{3} \nu^3, \nu \xi + \frac{1}{2} \frac{\xi^1}{\nu^1} \right).
\]

The direction cosines of the tangent plane are proportional to

\[
\left( \nu^3 - \frac{\xi^3}{\nu^2}, \xi, -\nu^2 \right).
\]

Hence if the line

\[
y = kx + l
\]
\[
z = mx + n
\]
is a tangent to the surface at this point, we have

\[
\frac{\xi^3}{\nu^2} + \frac{1}{3} \nu^3 = k\xi + l,
\]
\[
\nu \xi + \frac{1}{3} \frac{\xi^1}{\nu^1} = m\xi + n,
\]
\[
\nu^3 - \frac{\xi^3}{\nu^2} = -k\xi + m\nu^2,
\]

and therefore

\[
\frac{4}{3} \nu^3 = m\nu^2 + l,
\]
\[
\frac{3}{2} \nu^2 = k\frac{\xi^1}{\nu^1} + n.
\]
If the straight line is a bitangent, these equations are also satisfied when other values \( \xi, \nu_1 \) are put in the place of \( \xi, \nu \) respectively.

Hence \( \nu \) and \( \nu_1 \) are either the same root, or different roots of the equation

\[
\frac{4}{3} \nu^3 = m \nu^2 + l,
\]

that is,

\[
\nu = \nu_1,
\]

or else

\[
\nu + \nu_1 - \frac{\nu \nu_1}{\nu + \nu_1} = \frac{3}{4} m,
\]

and

\[
- \frac{\nu \nu_1^2}{\nu + \nu_1} = \frac{3}{4} l.
\]

Also \( \xi/\nu \) and \( \xi_1/\nu_1 \) are either the same or are different roots of the equation

\[
3 \left( \frac{\xi}{\nu} \right)^2 - 2k \left( \frac{\xi}{\nu} \right)^3 - 2n = 0,
\]

in which case

\[
\frac{\xi}{\nu} = - \frac{\xi_1}{\nu_1},
\]

or else

\[
\frac{\xi^2}{\nu^2} + \frac{\xi_1^2}{\nu_1^2} = \frac{3}{4} k,
\]

\[
\frac{\xi^2 \xi_1^2}{\nu^2 \nu_1^2} = - \frac{3}{4} n.
\]

The solution

\[
\nu = \nu_1, \quad \xi = \xi_1
\]

is irrelevant; the solution

\[
\nu = \nu_1, \quad \xi = - \xi_1
\]

gives the original congruency, and

gives

\[
\xi = \xi_1.
\]

A new series of bitangents is given by taking

\[
\frac{\xi}{\nu} = - \frac{\xi_1}{\nu_1}, \quad \nu \neq \nu_1.
\]

We have

\[
\nu^2 + \nu \nu_1 + \nu_1^2 = \frac{3}{4} m \left( \nu + \nu_1 \right),
\]

\[
\nu^2 \nu_1^2 = - \frac{3}{4} l \left( \nu + \nu_1 \right),
\]

\[
\frac{\xi^3}{\nu^3} - k \frac{\xi}{\nu} = \frac{l}{\nu} - \frac{1}{3} \nu^2,
\]

\[
\frac{\xi_1^3}{\nu_1^3} - k \frac{\xi_1}{\nu_1} = \frac{l}{\nu_1} - \frac{1}{3} \nu_1^2,
\]
whence
\[ l \left( \frac{1}{\nu} + \frac{1}{\nu_1} \right) = \frac{1}{3} (\nu^2 + \nu_1^2), \]
or
\[ -4\nu_1 = \nu^2 + \nu_1^2. \]
Hence we deduce that
\[ l = -\frac{1}{2} m^3. \]
The elimination of \( \xi \), by help of the equation
\[ 3(\xi/v)^4 - 2k(\xi/v)^2 - 2n = 0, \]
gives
\[ 8192n (k^3 - 2n) - 384km^4 (18n - k^3) - 243m^8 = 0. \]
These two equations, connecting \( k, l, m, n \), define the second congruency of bitangents to the surface.
A third is given by combining the equations
\[
\begin{align*}
\nu^2 + \nu_1^2 + \nu_1^3 &= \frac{2}{3} m (\nu + \nu_1), \\
\nu^3 \nu_1^2 &= -\frac{3}{2} l (\nu + \nu_1), \\
\xi^3 / \nu^2 + \xi_1^3 / \nu_1^3 &= \frac{2}{3} k, \\
\xi^3 / \nu_1^3 + \frac{1}{3} \nu_1^3 &= k \xi + l, \\
\xi_1^3 / \nu_1^3 + \frac{1}{3} \nu_1^3 &= k \xi_1 + l.
\end{align*}
\]
The result of elimination may be expressed by saying that the expression
\[ 256 \nu^3 + 9 \nu^2 (64m^4 - m^2) + 18 \nu (21m^6 - l^3) - 9l^3 (m^3 - 3l)^2 \]
contains the expression
\[ 27 \nu^3 - 2n (k^3 - 18kn) - 2n (k^3 - 2n)^2 \]
as a factor.
The surface has a nodal curve and a cuspidal curve. These are found by expressing the conditions that the equations
\[
\begin{align*}
y &= x^3 / \nu^2 + \frac{1}{5} \nu^3, \\
z &= \nu x + \frac{1}{5} x^3 / \nu^4,
\end{align*}
\]
solved for \( \nu \), may have a pair of common roots.
If the roots are different we have a nodal curve, to wit, the curve traced by the point
\[ (\frac{3}{4} \ell^5, \frac{4}{9} \ell^9, \frac{4}{8} \ell^6) \]
for different values of \( t \).
If the roots are equal we have the cuspidal curve traced by the point

\[(8\theta^5, \frac{1}{3}\theta^2\phi, 40\theta^6)\].

It is easily verified that the tangents to either of these curves are included in the third congruency of bitangents to the surface, and that accordingly the curves will satisfy the differential equations to that congruency.

The cuspidal curve on this surface has the property discussed above (§ 36), and it is for this reason that its tangents are included among the bitangents to the surface.

**Example IV.**—**Inflexional Congruencies.** (§§ 39 to 50.)

§ 39. When the two values of \(dc_1 : dc_2\) given by the equation \(db_1 dc_2 - dc_1 db_2 = 0\) (§ 28) coincide identically, the lines of the congruency are inflexional tangents to a surface.

For if the direction-cosines of the normal to a surface at the point \((x, y, z)\) are proportional to \(l, m, n\), the directions of the inflexional tangents are given by the equation

\[dxdl + dydm + dzn = 0.\]

Hence, from the last equation of § 29, we find that the directions of the inflexional tangents in that case are given by

\[d\lambda dy_3 = dx (dc_1 + \lambda dc_2 + c_3 d\lambda).\]

But the equation

\[
\begin{vmatrix}
  x + \frac{\partial b_1}{\partial c_1}, & \frac{\partial b_2}{\partial c_1} \\
  \frac{\partial b_1}{\partial c_2}, & x + \frac{\partial b_2}{\partial c_2}
\end{vmatrix} = 0
\]

has equal roots, so that

\[
x = - \frac{1}{2} \left( \frac{\partial b_1}{\partial c_1} + \frac{\partial b_2}{\partial c_2} \right),
\]

\[
\lambda \frac{\partial b_2}{\partial c_1} = - \frac{1}{2} \left( \frac{\partial b_1}{\partial c_1} - \frac{\partial b_2}{\partial c_2} \right),
\]

\[
xdc_2 + db_2 = \left( x + \frac{\partial b_2}{\partial c_2} \right) dc_2 + \frac{\partial b_2}{\partial c_1} dc_1
\]

\[= \frac{\partial b_1}{\partial c_1} (dc_1 + \lambda dc_2).\]

Thus

\[dy_3 - c_3 dx = \frac{\partial b_2}{\partial c_1} (dc_1 + \lambda dc_2),\]
and the above equation for the inflexional tangents becomes

\[(dy_2 - c_5dx) \left( \frac{dx_2}{dx_1} d\lambda - dx \right) = 0.\]

Hence one of them is parallel to the plane \( y_2 = c_5x. \)

But it must lie in the tangent plane and pass through the point of contact. It is, therefore, the line

\[
y_1 = c_1x + b_1, \\
y_2 = c_2x + b_2,
\]

which was to be proved.

It is remarkable that though from this point of view a congruency of inflexional tangents appears to be a particular kind of bitangential congruency, yet when they are considered from the point of view of the surface, the one is as general as the other, and every surface, whose degree is not 2 or 3, has one of each.

**Degenerate Inflexional Congruencies. (§ 40.)**

§ 40. An interesting question arises as to whether there is a degenerate form of the inflexional congruency when the surface it envelopes is replaced by a curve. In such a case the lines of the congruency that meet the curve at any one point will form a cone, and the cones belonging to consecutive points of the curve must not meet each other, for if they did they would envelope a surface, and the congruency would be of the bitangential kind. The only kind of conical surface that will meet the case is easily seen to consist of one or more planes touching the curve, and the congruency is made up as follows: Planes are drawn through the tangents to a curve according to some fixed law, and lines are drawn through the points of contact in each plane. The planes will envelope a torse on which the curve will lie, and thus the congruency may be said to consist of all the tangents to a surface at the points of a curve on that surface.

The existence of these two kinds of congruency appears to have been overlooked in the classification given by Salmon (‘Geometry of Three Dimensions,’ § 453). It might also be desirable to break up the first category given there into two, the bitangents to a surface and the bitangents to a torse, that is, the “lines in two planes” of a curve. The third category would then have to be divided into three, according as one, each, or neither, of the surfaces was developable, and the fourth into two.

**Consideration of the General Surface. (§§ 41–49.)**

§ 41. Take the surface

\[
\phi(x, y_1, y_2) = 0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1).
\]
The line

\[ y_1 = c_1x + b_1 \]  \hspace{1cm} (2)
\[ y_2 = c_2x + b_2 \]  \hspace{1cm} (3)

will be an inflexional tangent if the equations

\[ M = 0, \quad \partial M / \partial \mu = 0, \quad \partial^2 M / \partial \mu^2 = 0, \]

are satisfied together, where

\[ M \equiv \partial \phi / \partial (\mu, c_1x + b_1, c_2x + b_2). \]

By eliminating \( \mu \) and putting \( p_1 \) for \( c_1 \), \( y_1 - p_1x \) for \( b_1 \), \&c., we have two equations of Clairaut's form satisfied by the lines of the congruency.

§ 42. For the singular solutions we have

\[ xdc_1 + db_1 = 0 \]  \hspace{1cm} (4)
\[ xdc_2 + db_2 = 0 \]  \hspace{1cm} (5)
\[ \partial M / \partial c_1 dc_1 + \partial M / \partial c_2 dc_2 + \partial M / \partial b_1 db_1 + \partial M / \partial b_2 db_2 = 0, \quad \text{(because} \quad \partial M / \partial \mu = 0) \]  \hspace{1cm} (6)
\[ \partial M / \partial \mu / \partial c_1 dc_1 + \partial M / \partial \mu / \partial c_2 dc_2 + \partial M / \partial \mu / \partial b_1 db_1 + \partial M / \partial \mu / \partial b_2 db_2 = 0, \quad \text{(because} \quad \partial^2 M / \partial c^2 = 0) \]  \hspace{1cm} (7)
\[ \partial M / \partial \mu^2 / \partial c_1 dc_1 + \partial M / \partial \mu^2 / \partial c_2 dc_2 + \partial M / \partial \mu^2 / \partial b_1 db_1 + \partial M / \partial \mu^2 / \partial b_2 db_2 + \partial M / \partial \mu d\mu = 0 \]  \hspace{1cm} (8)

But

\[ \partial M / \partial c_1 = \mu \partial M / \partial b_1, \quad \partial M / \partial c_2 = \mu \partial M / \partial b_2. \]

Hence, by help of (4) and (5), (6) gives

\[ (\mu - x) \left( \frac{\partial M}{\partial b_1} dc_1 + \frac{\partial M}{\partial b_2} dc_2 \right) = 0, \]

and (7) gives

\[ (\mu - x) \left( \frac{\partial M}{\partial \mu} \frac{dc_1}{\partial b_1} + \frac{\partial M}{\partial \mu} \frac{dc_2}{\partial b_2} \right) + \frac{\partial M}{\partial b_1} dc_1 + \frac{\partial M}{\partial b_2} dc_2 = 0. \]

Therefore

\[ \frac{\partial M}{\partial b_1} dc_1 + \frac{\partial M}{\partial b_2} dc_2 = 0. \]
and either
\[ \mu = x \quad \text{or} \quad \frac{\partial^2 M}{\partial \mu^2} \, dc_1 + \frac{\partial^2 M}{\partial \mu \partial b_1} \, dc_1 = 0. \]

Also (8) becomes
\[ (\mu - x) \left\{ \frac{\partial^2 M}{\partial \mu^2 \partial b_1} \, dc_1 + \frac{\partial^2 M}{\partial \mu^2 \partial b_2} \, dc_2 \right\} + 2 \left\{ \frac{\partial^2 M}{\partial \mu \partial b_1} \, dc_1 + \frac{\partial^2 M}{\partial \mu \partial b_2} \, dc_2 \right\} + \frac{\partial^2 M}{\partial \mu^2} \, d\mu = 0. \]

§ 43. First, let \( \mu = x \). Then
\[ M = \phi(x, y_1, y_2) = 0, \]
\[ \frac{\partial M}{\partial \mu} = \frac{\partial \phi}{\partial x} + c_1 \frac{\partial \phi}{\partial y_1} + c_2 \frac{\partial \phi}{\partial y_2} = 0, \]
\[ \frac{\partial^2 M}{\partial \mu^2} = \frac{\partial^2 \phi}{\partial x^2} + 2c_1 \frac{\partial^2 \phi}{\partial x \partial y_1} + 2c_2 \frac{\partial^2 \phi}{\partial x \partial y_2} + c_1 c_2 \frac{\partial^2 \phi}{\partial y_1^2} + 2c_1 c_2 \frac{\partial^2 \phi}{\partial y_1 \partial y_2} + c_2 c_2 \frac{\partial^2 \phi}{\partial y_2^2} = 0, \]
\[ \frac{\partial M}{\partial b_1} \frac{dc_1}{dx} + \frac{\partial M}{\partial b_2} \frac{dc_2}{dx} = \frac{\partial \phi}{\partial y_1} \frac{dc_1}{dx} + \frac{\partial \phi}{\partial y_2} \frac{dc_2}{dx} = 0. \]

The last equation and the equation (8) are satisfied in virtue of the first three and the equations \( p_1 = c_1, p_2 = c_2 \).

The integral of these equations represents a series of curves on the surface \( \phi = 0 \), each tangent to each curve being an inflexional tangent to the surface.

\[ \text{Second Singular Solutions. (§§ 44, 45.)} \]

§ 44. If there is a singular solution of these equations, it is given by supposing two consecutive curves of the series to intersect. At their point of intersection the inflexional tangents will then be in the same direction, and the singular solution therefore appears to be the locus of parabolic points on the surface. We shall, however, find that this curve is not a solution at all in general. The consideration of the reciprocal surface suggests that a cuspidal curve may supply a solution. We begin with the parabolic curve.

We take, as a trial solution,
\[ \frac{\partial^2 \phi}{\partial x^2} + c_1 \frac{\partial^2 \phi}{\partial x \partial y_1} + c_2 \frac{\partial^2 \phi}{\partial x \partial y_2} = \kappa \frac{\partial \phi}{\partial x}, \]
\[ \frac{\partial^2 \phi}{\partial x \partial y_1} + c_1 \frac{\partial^2 \phi}{\partial y_1^2} + c_2 \frac{\partial^2 \phi}{\partial y_1 \partial y_2} = \kappa \frac{\partial \phi}{\partial y_1}, \]
\[ \frac{\partial^2 \phi}{\partial x \partial y_2} + c_1 \frac{\partial^2 \phi}{\partial y_1 \partial y_2} + c_2 \frac{\partial^2 \phi}{\partial y_2^2} = \kappa \frac{\partial \phi}{\partial y_2}. \]
In order to test whether this is a solution, we differentiate totally, multiply by 1, \(c_1\), \(c_2\), and add, and we have

\[
\left( \frac{\partial}{\partial x} + p_1 \frac{\partial}{\partial y_1} + p_2 \frac{\partial}{\partial y_2} \right) \left( \frac{\partial}{\partial x} + c_1 \frac{\partial}{\partial y_1} + c_2 \frac{\partial}{\partial y_2} \right) \phi + \frac{d_1}{dx} \cdot \kappa \frac{\partial \phi}{\partial y_1} + \frac{d_2}{dx} \cdot \kappa \frac{\partial \phi}{\partial y_2} = 0,
\]

where the dashes outside the brackets indicate that in differentiation \(c_1\) and \(c_2\) are to be treated as constants.

In this equation the substitution \(p_1 = c_1, p_2 = c_2\) will make the coefficient of \(\kappa\) disappear, but the other terms will generally not vanish, and therefore the locus of parabolic points is not generally a solution of the differential equations of the congruency.

It is, in fact, generally speaking, the cusp-locus of the first singular solution.

§ 45. Suppose, now, that the surface has a cuspidal curve. It may be shown that this is a solution.

For at any point \((x, y_1, y_2)\) on the surface, the equations

\[
y_1 = c_1 x + b_1, \quad y_2 = c_2 x + b_2, \quad M = 0, \quad \partial M / \partial \mu = 0, \quad \partial^2 M / \partial \mu^2 = 0
\]

are satisfied by putting

\[
\mu = x, \quad b_1 = y_1 - c_1 x, \quad b_2 = y_2 - c_2 x
\]

if \(c_1, c_2\) are determined by the equations

\[
\frac{\partial \phi}{\partial x} + c_1 \frac{\partial \phi}{\partial y_1} + c_2 \frac{\partial \phi}{\partial y_2} = 0,
\]

\[
2 c_1 \frac{\partial^2 \phi}{\partial x \partial y_1} + 2 c_2 \frac{\partial^2 \phi}{\partial x \partial y_2} + c_1 \frac{\partial^2 \phi}{\partial y_1^2} + 2 c_1 c_2 \frac{\partial^2 \phi}{\partial y_1 \partial y_2} + c_2 \frac{\partial^2 \phi}{\partial y_2^2} = 0.
\]

From the latter may be deduced, by differentiation, on the supposition that \(dx = dy_1 / c_1 = dy_2 / c_2\), which is consistent with \(\phi = 0\), that

\[
\left( \frac{\partial}{\partial x} + c_1 \frac{\partial}{\partial y_1} + c_2 \frac{\partial}{\partial y_2} \right)^2 \phi + 2 \left( \frac{\partial^2 \phi}{\partial x \partial y_1} + c_1 \frac{\partial^2 \phi}{\partial y_1^2} \right) \left( \frac{\partial^2 \phi}{\partial x \partial y_2} + c_2 \frac{\partial^2 \phi}{\partial y_2^2} \right) + 2 \left( \frac{\partial c_1}{\partial x} + c_1 \frac{\partial c_1}{\partial y_1} + c_2 \frac{\partial c_1}{\partial y_2} \right) = 0.
\]

The equation (9) holds all over the surface.

Now, at a singular point where there are two coincident tangent planes,

\[
\frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial \nu} = \frac{\partial \phi}{\partial y_2} = 0,
\]
and
\[
\left( \frac{\partial}{\partial x} + c_1 \frac{\partial}{\partial y_1} + c_2 \frac{\partial}{\partial y_2} \right)^2 \phi
\]
is a perfect square, so that the first equation for \( c_1 \) and \( c_2 \) is nugatory, and the second may be written in any of the forms
\[
\begin{align*}
\frac{\partial^3 \phi}{\partial x^2} + c_1 \frac{\partial^3 \phi}{\partial x \partial y_1} + c_2 \frac{\partial^3 \phi}{\partial x \partial y_2} &= 0, \\
\frac{\partial^3 \phi}{\partial x \partial y_1} + c_1 \frac{\partial^3 \phi}{\partial y_1^2} + c_2 \frac{\partial^3 \phi}{\partial y_1 \partial y_2} &= 0, \\
\frac{\partial^3 \phi}{\partial x \partial y_2} + c_1 \frac{\partial^3 \phi}{\partial y_2^2} + c_2 \frac{\partial^3 \phi}{\partial y_2^3} &= 0.
\end{align*}
\]

The equation (9) will therefore not contain the differential coefficients of \( c_1 \) and \( c_2 \), but will be available to determine \( c_1 \) and \( c_2 \) themselves.

If there is a cuspidal edge these things hold at every point of it. Let \( m_1, m_2 \) be the values of \( p_1, p_2 \) taken along the edge, and let us write \( D \) for the operator
\[
\frac{\partial}{\partial x} + m_1 \frac{\partial}{\partial y_1} + m_2 \frac{\partial}{\partial y_2}.
\]
Also we may put
\[
\frac{\partial^3 \phi}{\partial x^2} = \lambda^2, \quad \frac{\partial^3 \phi}{\partial x \partial y_1} = \lambda \mu_1, \quad \frac{\partial^3 \phi}{\partial x \partial y_2} = \lambda \mu_2, \quad \frac{\partial^3 \phi}{\partial y_1^2} = \mu_1^2, \quad \frac{\partial^3 \phi}{\partial y_1 \partial y_2} = \mu_1 \mu_2, \quad \frac{\partial^3 \phi}{\partial y_2^2} = \mu_2^2.
\]
The equations giving the inflexional tangents are then
\[
\lambda + \mu_1 p_1 + \mu_2 p_2 = 0.
\]
\[
\begin{align*}
\frac{\partial^3 \phi}{\partial x^3} + 3p_1 \frac{\partial^3 \phi}{\partial x^2 \partial y_1} + 3p_2 \frac{\partial^3 \phi}{\partial x^2 \partial y_2} + 3p_1^2 \frac{\partial^3 \phi}{\partial x \partial y_1^2} + 6p_1 p_2 \frac{\partial^3 \phi}{\partial x \partial y_1 \partial y_2} + 3p_2^2 \frac{\partial^3 \phi}{\partial x \partial y_2^2} \\
+ p_1^3 \frac{\partial^3 \phi}{\partial y_1^3} + 3p_1^2 p_2 \frac{\partial^3 \phi}{\partial y_1^2 \partial y_2} + 3p_1 p_2^2 \frac{\partial^3 \phi}{\partial y_1 \partial y_2^2} + p_2^3 \frac{\partial^3 \phi}{\partial y_2^3} &= 0.
\end{align*}
\]
We shall show that these two equations will, if \( p_1, p_2 \) are considered as coordinates, represent a plane cubic and one of its inflexional tangents.

We have
\[
D \frac{\partial^3 \phi}{\partial x^2} = 2\lambda D\lambda, \ \&c.
\]
Thus,
\[
\begin{align*}
D \frac{\partial^3 \phi}{\partial x^2} + 2m_1 D \frac{\partial^3 \phi}{\partial x \partial y_1} + 2m_2 D \frac{\partial^3 \phi}{\partial x \partial y_2} + m_1^2 D \frac{\partial^3 \phi}{\partial y_1^2} + m_1 m_2 D \frac{\partial^3 \phi}{\partial y_1 \partial y_2} + m_2^2 D \frac{\partial^3 \phi}{\partial y_2^2} \\
= 2 (\lambda + \mu_1 m_1 + \mu_2 m_2) (D\lambda + m_1 D\mu_1 + m_2 D\mu_2) \\
= 0,
\end{align*}
\]
for the first factor clearly vanishes, since \( \lambda, \mu_1, \mu_2 \) are proportional to the direction cosines of the tangent plane.

Also

\[
D \frac{\partial^2 \phi}{\partial x^2} + (m_1 + p_1) D \frac{\partial^2 \phi}{\partial x \partial y_1} + (m_2 + p_2) D \frac{\partial^2 \phi}{\partial y_2} + m_1 p_1 D \frac{\partial^2 \phi}{\partial y_1^2} + (m_1 p_2 + m_2 p_1) D \frac{\partial^2 \phi}{\partial y_1 \partial y_2} + m_2 p_2 D \frac{\partial^2 \phi}{\partial y_2^2} \\
= (\lambda + \mu_1 m_1 + \mu_2 m_2) (D\lambda + p_1 D\mu_1 + p_2 D\mu_2) \\
+ (\lambda + \mu_1 p_1 + \mu_2 p_2) (D\lambda + m_1 D\mu_1 + m_2 D\mu_2) \\
= (\lambda + \mu_1 p_1 + \mu_2 p_2) (D\lambda + m_1 D\mu_1 + m_2 D\mu_2),
\]

and

\[
D \frac{\partial^2 \phi}{\partial y^2} + 2p_1 D \frac{\partial^2 \phi}{\partial x \partial y_1} + 2p_2 D \frac{\partial^2 \phi}{\partial x \partial y_2} + p_1^2 D \frac{\partial^2 \phi}{\partial y_1^2} + 2p_1 p_2 D \frac{\partial^2 \phi}{\partial y_1 \partial y_2} + p_2^2 D \frac{\partial^2 \phi}{\partial y_2^2} \\
= (\lambda + \mu_1 p_1 + \mu_2 p_2) (D\lambda + p_1 D\mu_1 + p_2 D\mu_2).
\]

Thus the point \((m_1, m_3)\) lies on the cubic, its polar line is \( \lambda + \mu_1 p_1 + \mu_2 p_2 = 0 \), and its polar conic consists of this line and another. Hence the three solutions of the two equations coincide, and we have \( p_1 = m_1, p_2 = m_3 \).

Thus the cuspidal edge is enveloped by the inflexional tangents, and is a solution of the differential equation of the congruency.

If the surface has a nodal curve the equations \( M = 0, \partial M/\partial \mu = 0, \partial^2 M/\partial \mu^2 = 0 \) are apparently satisfied along it, but these equations, as they stand, are not enough to determine \( c_1 \) and \( c_2 \), and when \( c_1 \) and \( c_2 \) are evaluated by means of another differentiation they are not generally equal to \( p_1 \) and \( p_2 \) taken along the nodal curve. In fact there are two inflexional tangents in each sheet at every point, and the tangent to the nodal curve is not generally the same as any of the four. Hence the nodal curve, as such, is not a solution.\(^*\)

Another Second Singular Solution. (§ 46-49.)

§ 46. Let us now take the alternative of § 42 and suppose that

\[
\frac{\partial^2 M}{\partial \mu \partial c_1} dc_1 + \frac{\partial^2 M}{\partial \mu \partial c_2} dc_2 = 0.
\]

\(^*\) The lines that touch the surface at points on the nodal curve form such a degenerate inflexional congruency as was discussed above (§ 40), and they will satisfy the differential equations to the inflexional congruency of the surface in the unreduced form in which we have used them. The tangents to the nodal curve form a first singular solution included in the complete primitive, and the nodal curve belongs to the second singular solution which also includes the cuspidal edge of the torse enveloped by the tangent planes.
OF SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS.

Then as \(c_1\) and \(c_2\) are not both constant, we have \(N = 0\) where

\[
N = \frac{\partial^2 M}{\partial \mu \partial c_1} \frac{\partial M}{\partial c_2} - \frac{\partial^2 M}{\partial \mu \partial c_2} \frac{\partial M}{\partial c_1}.
\]

This is a further condition connecting \(b_1, b_2, c_1, c_2, \mu\). From it we deduce

\[
\frac{\partial N}{\partial c_1} dc_1 + \frac{\partial N}{\partial c_2} dc_2 + \frac{\partial N}{\partial b_1} db_1 + \frac{\partial N}{\partial b_2} db_2 + \frac{\partial N}{\partial \mu} d\mu = 0.
\]

From this and the former equations we can again eliminate the differentials. Suppose the resultant equation to be \(P = 0\). Then the equations \(N = 0, P = 0\) afford an integral of the differential equations. We will verify this.

§ 47. \(N = 0\) may be replaced by

\[
\frac{\partial M}{\partial b_1} C_1 + \frac{\partial M}{\partial b_2} C_2 = 0,
\]

\[
\frac{\partial M}{\partial \mu \partial b_1} C_1 + \frac{\partial M}{\partial \mu \partial b_2} C_2 = 0,
\]

where \(C_1\) and \(C_2\) do not both vanish.

Also \(P = 0\) may be replaced by

\[
\left(\frac{\partial N}{\partial c_1} - x^2 \frac{\partial N}{\partial b_1}\right) C_1 + \left(\frac{\partial N}{\partial c_2} - x^2 \frac{\partial N}{\partial b_2}\right) C_2 + \frac{\partial N}{\partial \mu} K = 0 \quad \ldots \quad (10),
\]

\[
(\mu - x) \frac{\partial M}{\partial \mu \partial c_1} C_1 + \left(\mu - x\right) \frac{\partial M}{\partial \mu \partial c_2} C_2 + \frac{\partial M}{\partial \mu^2} K = 0 \quad \ldots \quad (11).
\]

We have also \(M = 0, \frac{\partial M}{\partial \mu} = 0, \frac{\partial^2 M}{\partial \mu^2} = 0\).

The last three equations give

\[
\frac{\partial M}{\partial b_1} \left(\mu c_1' + b_1'\right) + \frac{\partial M}{\partial b_2} \left(\mu c_2' + b_2'\right) = 0,
\]

if we write \(c_1'\) for \(dc_1/dx, \&c\).

We may then put

\[
\mu c_1' + b_1' = uC_1, \mu c_2' + b_2' = uC_2.
\]

They also give

\[
\frac{\partial^2 M}{\partial \mu \partial b_1} uC_1 + \frac{\partial^2 M}{\partial \mu \partial b_2} uC_2 + c_1' \frac{\partial M}{\partial b_1} + c_2' \frac{\partial M}{\partial b_2} = 0,
\]
so that we may put

\[ c_1' = vC_1, \quad c_2' = vC_2, \]

\[ U_1' = (u - \mu v) C_1, \quad U_2' = (u - \mu v) C_2. \]

Further, they give

\[ \frac{\partial^2 M}{\partial \mu^2 \partial b_1} uC_1 + \frac{\partial^2 M}{\partial \mu^2 \partial b_2} uC_2 + 2 \frac{\partial^2 M}{\partial \mu \partial b_1} vC_1 + 2 \frac{\partial^2 M}{\partial \mu \partial b_2} vC_2 + \frac{\partial^2 M}{\partial \mu^3} \mu' = 0, \]

whence, by comparison with (11),

\[ uK = (\mu - x) \mu'. \]

Again, since \( N = 0 \),

\[ \frac{\partial^2 M}{\partial \mu_1} vC_1 + \frac{\partial^2 M}{\partial \mu_2} vC_2 + \frac{\partial^2 M}{\partial \mu_1} (u - \mu v) C_1 + \frac{\partial^2 M}{\partial \mu_2} (u - \mu v) C_2 + \frac{\partial^2 M}{\partial \mu \mu - x} = 0. \]

Multiply this by \( \mu - x \) and (10) by \( u \) and subtract. The equation connecting \( u \) and \( v \) is then found to be

\[ \{ u - v(\mu - x) \} \left( \frac{\partial^2 M}{\partial \mu_1} C_1 + \frac{\partial^2 M}{\partial \mu_2} C_2 - \mu \frac{\partial^2 M}{\partial \mu_1} C_1 - \mu \frac{\partial^2 M}{\partial \mu_2} C_2 \right) = 0. \]

Thus in general \( u - \mu v = - vx \), that is, \( c_1'x + b_1' = 0 = c_2'x + b_2' \) and the differential equations are satisfied.

§ 48. In the case when \( N = 0 \), \( P \neq 0 \), we still have

\[ dc_1 : dc_2 : : C_1 : C_2 : : db_1 : db_2, \]

but the ratio \( dc_1 : db_1 \) is unassigned.

The equation to the tangent plane to the surface at

\[ (\mu, c_1\mu + b_1, c_2\mu + b_2) \]

is, as always,

\[ (y_1 - c_1x - b_1) \frac{\partial M}{\partial b_1} + (y_2 - c_2x - b_2) \frac{\partial M}{\partial b_2} = 0. \]

Hence, when \( N = 0 \), the tangent plane at any adjacent point is

\[ (y_1 - c_1x - b_1) \left( \frac{\partial M}{\partial b_1} + d \frac{\partial M}{\partial b_1} \right) + (y_2 - c_2x - b_2) \left( \frac{\partial M}{\partial b_2} + d \frac{\partial M}{\partial b_2} \right) = 0. \]

Thus the tangent planes at all adjacent points pass through the same straight line

\[ \begin{align*}
 y_1 &= c_1x + b_1 \\
 y_2 &= c_2x + b_2
\end{align*} \]
Hence the point is a parabolic point on the surface, and the line of the congruency is the intersection of tangent planes at two consecutive parabolic points. All such lines will generate a torse, and they would belong to the first singular solution were they not already in the complete primitive.

§ 49. The intersection of two consecutive generators of this torse is given by the equations

\[
\begin{align*}
y_1 &= c_1x + b_1, \\
y_2 &= c_2x + b_2, \\
x &= -\frac{db_1}{dc_1} \text{ or } -\frac{db_2}{dc_2},
\end{align*}
\]

where \( b_1, c_1, b_2, c_2 \) are connected by the equations

\[
M = 0, \quad \partial M/\partial \mu = 0, \quad \partial^3 M/\partial \mu^2 = 0, \quad N = 0.
\]

These equations are satisfied if \( P = 0 \), and therefore the cuspidal edge of this torse is the second singular solution given by taking \( N = 0 = P \).

A Particular Example.  (§ 50.)

§ 50. As an example of an inflexional congruency, we may take the system of lines

\[
\begin{align*}
y &= 3a^2b^4x + \frac{1}{3}b^5(1 - 6a^3), \\
z &= b^3(1 + 2a^3)x - \frac{3}{2}a^3b^5.
\end{align*}
\]

These are half the system of inflexional tangents of the surface of § 38.

It is easily verified that the cuspidal curve is a second singular solution, and the nodal curve not.

The first singular solution is given by

\[
x = ab^5, \quad b = \text{constant}.
\]

It is

\[
\begin{align*}
y &= \frac{x^3}{b^5} + \frac{1}{3}b^5, \\
z &= \frac{1}{2} \frac{x^3}{b^{12}} + b^5x.
\end{align*}
\]

The system

\[
\begin{align*}
y &= (1 + \alpha^3) b^4 \frac{x}{a} - \frac{3}{2}b^5, \\
z &= 2b^5x + \frac{1}{2}a^3b^5 - ab^5,
\end{align*}
\]
which includes the other inflexional tangents to the same surface, would serve equally well.

This example shows that it is possible for the inflexional tangents to a surface to form two distinct congruencies. The parabolic and cuspidal curves, moreover, coincide.

Example V.—System of Curves in Space. (§§ 51, 52.)

§ 51. As another example, take the equations

\[
\frac{dx^2}{x^2 - 1} = \frac{dy^2}{y^2 - 1} = \frac{dz^2}{z^2 - 1}.
\]

The complete primitive is the result of eliminating \( t \) from

\[
2x = t + \frac{1}{t}, \quad 2y = at + \frac{1}{at}, \quad 2z = bt + \frac{1}{bt},
\]

\( a \) and \( b \) being the constants of integration.

The curves represented are conies touching the six planes

\[
x = \pm 1, \quad y = \pm 1, \quad z = \pm 1.
\]

The first singular solution includes six forms—

\[
x = \pm 1, \quad 2y = u + \frac{1}{u}, \quad 2z = cu + \frac{1}{cu};
\]

\[
y = \pm 1, \quad 2z = u + \frac{1}{u}, \quad 2x = cu + \frac{1}{cu};
\]

\[
z = \pm 1, \quad 2x = u + \frac{1}{u}, \quad 2y = cu + \frac{1}{cu};
\]

in each \( u \) is a variable parameter, and \( c \) an arbitrary constant. The curves represented are conies inscribed in the six faces of the cube contained by the planes

\[
x = \pm 1, \quad y = \pm 1, \quad z = \pm 1.
\]

The second singular solution consists of the twelve edges of this cube.

§ 52. If we seek the singular solutions by means of the differential equations, we take

\[
p^2 (x^2 - 1) - (y^2 - 1) = 0, \quad q^2 (x^2 - 1) - (z^2 - 1) = 0,
\]

and form the Jacobian with respect to \( p \) and \( q \).
OF SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS. 563

We thus find

\[ pq(x^2 - 1)^2 = 0, \]

whence

\[ x = \pm 1, \text{ or } y = \pm 1, \text{ or } z = \pm 1. \]

Any one of these is found to be a singular first integral, and to reduce the equations to one of the form

\[ p^2(x^2 - 1) = y^2 - 1, \]

which we have seen how to integrate.

The singular solution of this is again

\[ (x^2 - 1)(y^2 - 1) = 0. \]

System of Plane Curves. Another extension of Clairaut's Form. (§§ 53–55.)

§ 53. There is an extension of Clairaut's form to higher orders, with one dependent variable.

Write \( p_r \) for \( \frac{dy}{dx} \), so that \( p_0 \) will mean \( y \).

Then integration by parts gives \( r \) being \( \frac{\phi}{n} \),

\[
\left[ p_{n+1} x^r dx = x^p_0 p_n - r x^{r-1} p_{n-1} + r (r - 1) x^{r-2} p_{n-2} \ldots + (r - 1)! r! p_{n-r}. \right.
\]

Call this expression \( q_n \), and take the equation,

\[ \phi (q_0, q_1, q_2 \ldots q_s) = 0. \]

This may be solved at once by differentiating; since

\[ dq_r/dx = x^r p_{n+1}, \]

we have

\[
p_{n+1} \left\{ \frac{\partial \phi}{\partial q_0} + x \frac{\partial \phi}{\partial q_1} + x^2 \frac{\partial \phi}{\partial q_2} + \ldots + x^r \frac{\partial \phi}{\partial q_s} \right\} = 0.
\]

The first factor gives the complete primitive, which consists of the equations,

\[ q_0 = a_0, \quad q_1 = a_1, \ldots q_s = a_s, \]

where \( a_0, a_1 \ldots a_s \) are constants, connected by the relation

\[ \phi (a_0, a_1, \ldots a_s) = 0, \]

but otherwise arbitrary.

The value of \( y \) may be found as follows—in the equation

\[ a_r x^{n-r} = p_{n-r} x^n - r p_{n-1} x^{n-1} + r (r - 1) p_{n-2} x^{n-2} \ldots \]

take differences with respect to \( r \); thus

\[
\Delta^s a_r x^{n-r} = (-1)^s s! x^{n-s} p_{n-s} + (-1)^{s+1} 2.3 \ldots (s + 1) r x^{n-s-1} p_{n-s-1} + \ldots.
\]

\[
4 \text{ c 2}
\]
Put now \( s = n, \ r = 0 \), and we have finally
\[
( - 1)^n n! \ y = \Delta^n a_0 x^{n-\theta} = a_n - n a_{n-1} x + \frac{n(n - 1)}{2!} a_{n-2} x^2 + \cdots + ( - 1)^s a_0 x^s,
\]
the constants being connected by the relation
\[
\phi (a_0, a_1, \ldots, a_n) = 0.
\]

§ 54. The factor
\[
\frac{\partial \phi}{\partial q_0} + x \frac{\partial \phi}{\partial q_1} + \cdots + x^n \frac{\partial \phi}{\partial q_n},
\]
equated to zero, leads to the singular solutions, the first integral being found by elimination of \( p_n \) from \( \phi = 0 \) by means of it.

Thus the solution of \( \phi (q_0, q_1, \ldots, q_n) = 0 \) is exactly on the lines of that of \( \psi (x_0 - y, p_1) = 0 \), which is Clairaut's form.

§ 55. The equations to be integrated in finding the singular solutions are
\[
\frac{da_1}{da_0} = \frac{da_2}{da_1} = \frac{da_3}{da_2} = \cdots = \frac{da_n}{da_{n-1}} (\ = x),
\]
\[
\phi (a_0, a_1, \ldots, a_n) = 0.
\]

For example, when \( n = 2 \), we have
\[
da_1^2 = da_0 \cdot da_2,
\]
\[
\phi (a_0, a_1, a_2) = 0.
\]

If \( (a_0, a_1, a_2) \) are taken as Cartesian coordinates, the solution represents curves on the surface \( \phi = 0 \), the tangents to which are parallel to generators of the cone \( a_1^2 = a_0 a_2 \), that is to say, meet a certain curve at infinity. The second singular solution is given by forming the envelope of such curves, which does not generally exist, but may in particular cases.

*Example VI. (§ 56.)*

§ 56. As an example take the equation
\[
(2y p_2 - p_1^2)^3 = 4 p_2 (p_1 - x p_2)^3, \text{ or } (q_0 t_2 - q_1^2)^3 + 4 q_0 t_1^3 = 0, \ n \text{ being } 2.
\]
The complete primitive is
\[
4 a c^3 y = 1 + 2c + 4 a^2 c^2 x + 4 a^4 c^3 x^3.
\]
The equations giving singular solutions are
\[
(1 + 6 a^2 c^2 x) \cdot da + 6 a^3 c^2 x \cdot dc = 0,
\]
\[
\left( x - \frac{1 + 2c}{2 a^2 c^3} \right) \cdot da - \frac{3 + 4c}{2 a^4} \cdot dc = 0.
\]
The result of eliminating $x$ is

$$c^3 da^2 + 3 (c da + adc) \{ (1 + 2c) c da + (3 + 4c) a dc \} = 0.$$  

The complete primitive of this is

$$a^2 - 6ac^3a - 6a^2c^3 = 0,$$

and for the singular solution of it we must take

$$a = 3ac^3 = -2ac.$$

The solutions $a = 0$, $c = 0$ arise by giving $a$ the particular value zero, and the true singular solution is

$$2 + 3c = 0.$$  

Hence for the first singular solution

$$a^2 - 6ac^3a - 6a^2c^3 = 0,$$

$$a^2 xy - 3a^2x + 3ay - 1 = 0.$$  

For the second

$$x = y^2.$$  

This is the equation to a parabola.

The curves of the first singular system are hyperbolas, having their asymptotes parallel to the axes of coordinates and having contact of the second order with this parabola.

The complete primitive represents a series of parabolas with axes parallel to the axis of $y$, and each having contact of the second order with some one of the hyperbolas, and, in fact, with two of them, since $a$ is given in terms of $a$ and $c$ by a quadratic equation.

§ 57. In order to make up further examples we only need to take:—

1. A curve $A$.

2. A series of curves $A_1$, depending on one parameter, each having contact of order $n$ with the curve $A$.

3. A series of curves $A_n$, involving two parameters, each having contact of order $n$ with some one of the curves $A_1$, and so on, till we have a series of curves $A_n$, involving $n$ parameters, each having contact of order $n$ with some one of the curves $A_{n-1}$.

Then $A_n$ is the complete primitive of a differential equation of order $n$, $A_{n-1}$ will be a first singular solution, $A_{n-1}$ an $n$th singular solution.
XV. *On the Ratio of the Specific Heats of Some Compound Gases.*


*Communicated by Professor J. J. Thomson, F.R.S.*

Received January 25,—Read February 14, 1895.

§ 1. *Introduction.*

The experiments to be described in the present paper are a continuation of those of which I gave an account in the 'Phil. Trans.,' vol. 185, p. 1.

It is shown there, from experiments on methane, ethane, and propane, and their derivatives, that the monohalogen derivatives of any one paraffin have in the gaseous state the same ratio of the specific heats, and that this ratio is the same as that of the hydrocarbon itself in two of the three series. Methane proved to be an exception, having a higher ratio than its derivatives.

It seemed to be a matter of some interest to find whether the same was true of unsaturated hydrocarbons and their monohalogen derivatives, and also to find the effect of introducing more than one halogen atom into the molecule. The aim of most of the experiments described below was to get information on these two points.

It is not necessary to give a detailed account of the apparatus and method of procedure, since they were the same as those described in the paper mentioned above. Kundt's dust-figure apparatus was used for finding the ratio of the wave-lengths of sound of a given pitch in air and in the gas under investigation, and the ratio of the specific heats was calculated by means of the formula

\[ \gamma = 1.408 \times \rho \times \left( \frac{l}{l'} \right)^2 \left( 1 + \frac{1}{\rho} \frac{d}{d\rho} \rho \right); \]

where \( \rho \) is the specific gravity of the gas referred to air, \( l \) and \( l' \) the lengths of the dust-figures in the gas and in air respectively, and the last factor is the correction for the deviation of the gas from Boyle's Law.

The vapour density of the gas was found experimentally at several different pressures, and from the curve plotted from the results \( \rho \) and the correction factor were determined in the way previously described.

Some of the substances used in this investigation are very difficult to purify, hence it is a matter of importance that when \( \gamma \) is determined in the way described, the
result is only very slightly affected by the presence of a little impurity. Impurities make themselves felt mainly by their modifying the density of the gas, and error from this source is avoided by the vapour density determination having been made in nearly every case on the same samples of the material as were used in the velocity of sound experiments. Hence impurity only has an effect in so far as the $\gamma$ of the foreign substance is not the same as that of the gas under investigation. An estimate of the amount of this error can be got by an application of equation (5) of my former paper. If, for instance, the methylene chloride contained 1 per cent. of chloroform, the error in $\gamma$ would be less than one part in a thousand.

Except where the contrary is stated, the materials were obtained from Kahlbaum and were dried and fractionated before being used. The following table of the observed range of boiling-points of definite quantities of the liquids as actually employed in the experiments will give some indication of the degree of purity obtained.

<table>
<thead>
<tr>
<th>Name</th>
<th>Quantity</th>
<th>B. P. (uncorrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene chloride</td>
<td>50 c.c.</td>
<td>43°5 to 44°3</td>
</tr>
<tr>
<td>Chloroform</td>
<td>300 c.c.</td>
<td>69°8 „ 61°2</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>50 c.c.</td>
<td>78°8 „ 76°9</td>
</tr>
<tr>
<td>Ethylene chloride</td>
<td>60 c.c.</td>
<td>83°9 „ 84°1</td>
</tr>
<tr>
<td>Ethylidene chloride</td>
<td>40 c.c.</td>
<td>59 „ 60°1</td>
</tr>
<tr>
<td>Allyl chloride</td>
<td>110 c.c.</td>
<td>45 „ 46°5</td>
</tr>
<tr>
<td>Allyl bromide</td>
<td>70 c.c.</td>
<td>69 „ 71</td>
</tr>
<tr>
<td>Ethyl formate</td>
<td>200 c.c.</td>
<td>56</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>400 c.c.</td>
<td>56 to 57°5</td>
</tr>
<tr>
<td>Carbon bisulphide</td>
<td>250 c.c.</td>
<td>46°8 „ 47</td>
</tr>
</tbody>
</table>

As regards the degree of accuracy attainable in the measurements I must again refer to my former paper. On p. 11 is given a typical set of measurements of the dust figures, and on p. 27 a series of experiments on ethyl chloride that afford a test of the accuracy of the vapour density determinations.

The experiments on carbon dioxide (Table XXII., below) show further, that whilst the work was in progress no change took place in the apparatus that affected the results. The first three experiments on carbon dioxide were made when the apparatus was first set up; the last three were made two years later, after it had been repeatedly dismantled for cleaning, and repairs and most of the original tubes had been replaced by others. The two sets of three give almost identical results.

Many of the gases used in the experiments have low saturation pressures at the atmospheric temperature—a fact which tends to increase the experimental error, for small errors in reading the height of the mercury column in the vapour density apparatus have a more serious effect when the total pressure to be measured is small, and in addition to this, the small range of pressure available makes it difficult to
draw the isothermal curve accurately. Hence the vapour-density determinations in some cases give a rather irregular curve, but when the divergences are so great as to leave much doubt how the curve should be drawn, I have made a separate determination of the relative densities in the way described under ethyl chloride in my former paper.

The column headed $\beta$ in the tables below, gives the ratio of the rates of increase with rise of temperature of the internal energy of the molecule and its kinetic energy of translation.

The usual equation connecting $\beta$ and $\gamma$, viz.,

$$\beta + 1 = \frac{2}{3(\gamma - 1)},$$

is deduced on the assumption that the gas is perfect, for it neglects the change of potential energy due to separation of the molecules on expansion, and assumes that $pv$ is proportional to $t$.

For air and a few other gases this is a matter of no consequence, but when we come to vapours not far removed from saturation, it is necessary to use a better formula, or at least to find whether the error made by using the old one is serious compared with the experimental error.

Since, to a first approximation, $pv$ is equal to $Rt$, we may write the characteristic equation in the form

$$pv = Rt + f(p, \dot{v}, t). \ldots \ldots \ldots \ldots (1),$$

where $f$ is so small that its square and the squares of its differential coefficients can be neglected.

Now we know from thermodynamics that

$$C_p - C_v = t \left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dt}\right)_p \ldots \ldots \ldots (2),$$

and from equation (1) we get by differentiating at constant volume and pressure respectively

$$\left(\frac{dp}{dt}\right)_v = \frac{R + df/dt}{v - df/dp},$$

$$\left(\frac{dv}{dt}\right)_p = \frac{R + df/dt}{p - df/dv}.$$

Hence

$$C_p - C_v = \frac{t \left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dt}\right)_p}{(p - df/dv)(v - df/dp)}$$

$$= \frac{R^2 t}{pv} \left(1 + \frac{1}{p} \frac{df}{dv} + \frac{1}{v} \frac{df}{dp} + \frac{2}{R} \frac{df}{dt}\right).$$
neglecting squares of the differential coefficients, or, since

$$C_p - C_v = R \left( 1 - \frac{f}{pv} \right) \left( 1 + \frac{1}{p} \frac{df}{dv} + \ldots \right)$$

$$= R \left( 1 + \frac{1}{p} \frac{df}{dv} + \frac{1}{v} \frac{df}{dp} + \frac{2}{R} \frac{df}{dt} \frac{1}{pv} \right). \quad \ldots (3)$$

If $\delta r$ is the increase of the kinetic energy of translation of the molecules in unit mass of the gas for a rise of temperature $\delta t$, we have

$$C_v \delta t = \delta r + \beta \delta r$$

$$= \frac{3}{2} (1 + \beta) R \delta t,$$

since

$$\frac{\delta r}{\delta t} = R \Delta t.$$

Hence

$$R = \frac{3}{2} \frac{C_v}{1 + \beta},$$

and dividing out $C_v$, equation (3) becomes

$$\gamma - 1 = \frac{2}{3 (1 + \beta)} \left( 1 + \frac{1}{p} \frac{df}{dv} + \frac{1}{v} \frac{df}{dp} + \frac{2}{R} \frac{df}{dt} \frac{1}{pv} \right). \quad \ldots (4).$$

If the form of $f(p, v, t)$ were known we could readily put equation (4) into a form fitted for calculation. Unfortunately we cannot use the characteristic equations proposed by Clausius, Van der Waals, Tait, and others, for the constants of these equations are not known except for a few gases.

There is however not much lost by taking an approximate value of the term in brackets, for from the nature of the equation the experimental error in $\gamma$ is considerably increased in $\beta$.

By differentiating the approximate equation

$$\beta + 1 = \frac{3}{2} \frac{1}{\gamma - 1}$$

we get

$$\frac{\delta \beta / \delta \gamma}{\beta / \gamma} = - \frac{2\gamma}{(\gamma - 1) (5 - 3\gamma)}.$$

Hence, if

$$\gamma = 1.3 \quad \quad \frac{\delta \beta / \delta \gamma}{\beta / \gamma} = - 8$$

$$= 1.2 \quad = - 9$$

$$= 1.1 \quad = - 12$$
Thus, since any error in $\gamma$ is increased tenfold in $\beta$, it is useless to do much more than find roughly the magnitude of the correction, until our experimental methods for determining $\gamma$ are much improved.

If we take Clausius’ equation

$$P = \frac{RT}{v - a} - \frac{C}{T(v + b)^2}$$

as the characteristic equation of a gas, we can, by making certain approximations, express the correction for $\beta$ in terms of

$$\frac{1}{P} \frac{d}{dv} (pv).$$

At ordinary temperatures and pressures $a$ and $b$ are negligible compared with $v$, so that $f$ may be taken to be $- C/Tv$.

Hence

$$\frac{1}{P} \frac{d}{dv} f = \frac{C}{Tpv^2} = \frac{C}{RT^2v}$$

and

$$\frac{1}{P} \frac{d}{dv} f = 0.$$

Therefore

$$\beta + 1 = \frac{2}{3(\gamma - 1)} \left[ 1 + \frac{4C}{RT^2v} \right]$$

and

$$\frac{1}{P} \frac{d}{dv} (pv) = \frac{C}{Tpv^2} = \frac{C}{RT^2v}.$$

Hence

$$\beta + 1 = \frac{2}{3(\gamma - 1)} \left[ 1 + \frac{4}{P} \frac{d}{dv} (pv) \right]. \quad (5)$$

Equation (5) has been used in calculating $\beta$ in all the tables that follow.

In my former paper I pointed out (p. 34) that the $\gamma$ of ethyl chloride and a few other gases appeared to be greater at the higher pressures, and mentioned that the effect might be due merely to the divergence of the gas from Boyle’s law, and not to any change in the value of $\beta$. This appears to be the case, for if $\beta$ is calculated from the results by means of formula (5), the progressive change disappears. The table below shows this for ethyl chloride, where the change in $\gamma$ is most marked.
Table II.

<table>
<thead>
<tr>
<th>$p$ (millims.)</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.180</td>
<td>2.878</td>
</tr>
<tr>
<td>205</td>
<td>1.180</td>
<td>2.878</td>
</tr>
<tr>
<td>285</td>
<td>1.189</td>
<td>2.751</td>
</tr>
<tr>
<td>295</td>
<td>1.180</td>
<td>2.939</td>
</tr>
<tr>
<td>400</td>
<td>1.191</td>
<td>2.754</td>
</tr>
<tr>
<td>400</td>
<td>1.183</td>
<td>2.814</td>
</tr>
<tr>
<td>410</td>
<td>1.184</td>
<td>2.896</td>
</tr>
<tr>
<td>560</td>
<td>1.193</td>
<td>2.797</td>
</tr>
<tr>
<td>610</td>
<td>1.190</td>
<td>2.858</td>
</tr>
<tr>
<td>630</td>
<td>1.192</td>
<td>2.818</td>
</tr>
</tbody>
</table>

The values of $\beta$ naturally diverge more widely from the mean than do those of $\gamma$, but there is no longer any progressive change to be seen, and we may conclude that the ratio of internal to translational energy of a molecule does not depend on the average distance between the molecules.

§ 2. Methylene Chloride. \((\text{CH}_2\text{Cl}_2)\)

Table III. gives the results of five determinations of the vapour-density of methylene chloride. The first column gives the pressure to the nearest millimetre at which the experiment was made, the second column gives the temperature, and the third gives the specific gravity of the gas referred to air at the same temperature and pressure.

Fig. 1 shows the curve plotted from the results.

Table III.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>19.2</td>
<td>3.081</td>
</tr>
<tr>
<td>155</td>
<td>18.6</td>
<td>3.087</td>
</tr>
<tr>
<td>160</td>
<td>18.9</td>
<td>3.086</td>
</tr>
<tr>
<td>199</td>
<td>18.6</td>
<td>3.094</td>
</tr>
<tr>
<td>211</td>
<td>18.7</td>
<td>3.096</td>
</tr>
</tbody>
</table>

Fig. 1.
Table IV. gives the final results calculated from three determinations of the velocity of sound in the vapour.

The letters at the heads of the columns have the following meanings:—

\( p \). The pressure of the vapour in the Kundt apparatus when the dust figures were made.

\( t \). The temperature of the vapour.

\( l \). The length of the dust figures in methylene chloride.

\( l' \). " " " air.

\( p' \). The specific gravity of the vapour at the pressure at which the experiment was made. This specific gravity was taken from the curve in fig 1.

\( 1 + \frac{1}{p} \frac{d}{dv} \frac{P}{p} \). The correction for deviation from Boyle's Law, calculated as described in my former paper.

\( \gamma \). The ratio of the specific heats, calculated by means of the formula on p. 567.

\( \beta \). The ratio of the rates of increase of internal and translational energy of the molecule with rise of temperature, calculated by formula (5) on p. 571.

### Table IV.

<table>
<thead>
<tr>
<th>( p )</th>
<th>( t )</th>
<th>( l )</th>
<th>( l' )</th>
<th>( p' )</th>
<th>( 1 + \frac{1}{p} \frac{d}{dv} \frac{P}{p} )</th>
<th>( \gamma )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>16-7</td>
<td>25-57</td>
<td>48-66</td>
<td>3-085</td>
<td>1-011</td>
<td>1-213</td>
<td>2-263</td>
</tr>
<tr>
<td>160</td>
<td>19-2</td>
<td>25-76</td>
<td>48-90</td>
<td>3-086</td>
<td>1-011</td>
<td>1-219</td>
<td>2-174</td>
</tr>
<tr>
<td>174</td>
<td>19-3</td>
<td>25-81</td>
<td>48-90</td>
<td>3-089</td>
<td>1-011</td>
<td>1-225</td>
<td>2-089</td>
</tr>
</tbody>
</table>

Mean ... ... 1-219 2-175

### §3. Chloroform, CHCl₃.

The tables and figures have in this and most of the succeeding cases the same meaning as in the case of methylene chloride.

### Table V.

<table>
<thead>
<tr>
<th>( p )</th>
<th>( t )</th>
<th>( p' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>19-4</td>
<td>4-112</td>
</tr>
<tr>
<td>106</td>
<td>21-2</td>
<td>4-114</td>
</tr>
<tr>
<td>121</td>
<td>20-6</td>
<td>4-119</td>
</tr>
<tr>
<td>138</td>
<td>20-3</td>
<td>4-128</td>
</tr>
</tbody>
</table>
DR. J. W. CAPSTICK ON THE RATIO OF THE

Fig. 2.

![Graph with data points and lines]

**Table VI.**

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$l$</th>
<th>$l'$</th>
<th>$p'$</th>
<th>$1 + \frac{1}{p} \frac{d}{dv}$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>20</td>
<td>21.78</td>
<td>48.96</td>
<td>4.114</td>
<td>1.008</td>
<td>1.150</td>
<td>3.581</td>
</tr>
<tr>
<td>114</td>
<td>21</td>
<td>21.81</td>
<td>49.05</td>
<td>4.116</td>
<td>1.010</td>
<td>1.157</td>
<td>3.414</td>
</tr>
<tr>
<td>121</td>
<td>19.8</td>
<td>21.69</td>
<td>48.95</td>
<td>4.118</td>
<td>1.012</td>
<td>1.152</td>
<td>3.593</td>
</tr>
</tbody>
</table>

Means . . . . 1.154 3.506


**Table VII.**

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$p'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>21.7</td>
<td>5.330</td>
</tr>
<tr>
<td>64</td>
<td>21.6</td>
<td>5.352</td>
</tr>
<tr>
<td>69</td>
<td>19.05</td>
<td>5.350</td>
</tr>
<tr>
<td>69</td>
<td>18.8</td>
<td>5.339</td>
</tr>
<tr>
<td>77</td>
<td>19.2</td>
<td>5.358</td>
</tr>
<tr>
<td>86</td>
<td>20.1</td>
<td>5.308</td>
</tr>
</tbody>
</table>

![Graph with data points and lines]
SPECIFIC HEATS OF SOME COMPOUND GASES.

Table VIII.

<table>
<thead>
<tr>
<th>p</th>
<th>t</th>
<th>l</th>
<th>(v)</th>
<th>(\rho)</th>
<th>(1 + \frac{1}{p} \frac{d}{dv} p)</th>
<th>(\gamma)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>20.6</td>
<td>18.86</td>
<td>49.02</td>
<td>5.332</td>
<td>1.012</td>
<td>1.125</td>
<td>4.585</td>
</tr>
<tr>
<td>72</td>
<td>20.2</td>
<td>18.85</td>
<td>49.00</td>
<td>5.351</td>
<td>1.014</td>
<td>1.131</td>
<td>4.367</td>
</tr>
<tr>
<td>73</td>
<td>20.2</td>
<td>18.87</td>
<td>49.00</td>
<td>5.354</td>
<td>1.014</td>
<td>1.133</td>
<td>4.285</td>
</tr>
<tr>
<td>75</td>
<td>20.5</td>
<td>18.83</td>
<td>49.01</td>
<td>5.356</td>
<td>1.014</td>
<td>1.130</td>
<td>4.409</td>
</tr>
</tbody>
</table>

Mean . . . . 1.130 4.411

§ 5. Ethylidene Chloride \((\text{CH}_3\text{CHCl})\).

Table IX.

<table>
<thead>
<tr>
<th>p</th>
<th>t</th>
<th>(\rho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td>23.6</td>
<td>3.439</td>
</tr>
<tr>
<td>138</td>
<td>25</td>
<td>3.446</td>
</tr>
<tr>
<td>146</td>
<td>23.8</td>
<td>3.447</td>
</tr>
<tr>
<td>153</td>
<td>24</td>
<td>3.451</td>
</tr>
</tbody>
</table>

Fig. 4.

Table X.

<table>
<thead>
<tr>
<th>p</th>
<th>t</th>
<th>l</th>
<th>(v)</th>
<th>(\rho)</th>
<th>(1 + \frac{1}{p} \frac{d}{dv} p)</th>
<th>(\gamma)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>21</td>
<td>23.50</td>
<td>49.03</td>
<td>3.440</td>
<td>1.013</td>
<td>1.127</td>
<td>4.518</td>
</tr>
<tr>
<td>132</td>
<td>24</td>
<td>23.74</td>
<td>49.36</td>
<td>3.443</td>
<td>1.014</td>
<td>1.137</td>
<td>4.183</td>
</tr>
<tr>
<td>138</td>
<td>23.9</td>
<td>23.73</td>
<td>49.34</td>
<td>3.445</td>
<td>1.015</td>
<td>1.139</td>
<td>4.079</td>
</tr>
</tbody>
</table>

Mean . . . . 1.134 4.243
§ 6. Ethylene Chloride (CH₂Cl·CH₂Cl).

Ethylene Chloride boils at 85°, and its vapour-pressure at ordinary temperature is so low, that small errors in reading the height of the mercury columns, or, in weighing the liquid, have too great an effect to allow a reliable curve to be drawn from the vapour-density determinations. Consequently these determinations were all made near the same pressure, and the mean of the results was used in the final calculations.

The values found were as follows:—

**Table XI.**

<table>
<thead>
<tr>
<th>p</th>
<th>t</th>
<th>ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.9</td>
<td>23</td>
<td>3.460</td>
</tr>
<tr>
<td>46.1</td>
<td>24</td>
<td>3.442</td>
</tr>
<tr>
<td>46.1</td>
<td>23.8</td>
<td>3.437</td>
</tr>
<tr>
<td>45.7</td>
<td>24.4</td>
<td>3.448</td>
</tr>
<tr>
<td>43.8</td>
<td>22.8</td>
<td>3.443</td>
</tr>
</tbody>
</table>

To find the value of the correction factor a determination of the relative densities at three pressures was made with the apparatus described under Ethyl Chloride in my former paper. The experiment was made at 24°, with the result shown in Table XII.

**Table XII.**

<table>
<thead>
<tr>
<th>ρ</th>
<th>ρc</th>
</tr>
</thead>
<tbody>
<tr>
<td>122.00</td>
<td>37.40</td>
</tr>
<tr>
<td>91.17</td>
<td>49.83</td>
</tr>
<tr>
<td>66.57</td>
<td>67.88</td>
</tr>
</tbody>
</table>

This gives 1.017 as the value of the correction factor at 45 millims.

Finally, Table XIII. gives the details of the velocity of sound determinations.

**Table XIII.**

<table>
<thead>
<tr>
<th>p</th>
<th>t</th>
<th>ρ</th>
<th>( l + \frac{1}{\rho} \frac{d\rho}{dv} )</th>
<th>γ</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>19.4</td>
<td>23.56</td>
<td>48.92</td>
<td>3.446</td>
<td>1.017</td>
</tr>
<tr>
<td>42</td>
<td>18.8</td>
<td>23.46</td>
<td>48.90</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>48</td>
<td>19.4</td>
<td>23.44</td>
<td>48.92</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Mean 1.137 4.184
§ 7. Ethylene (C₂H₄).

For the material I was indebted to the kindness of Professor Dewar, who gave me a cylinder of compressed ethylene. As the critical temperature of ethylene is near the ordinary atmospheric temperature, the bottle was placed in a freezing mixture to ensure the contents being liquefied, and so to keep back by fractional distillation any ether and water that had escaped the preliminary washing and drying of the gas.

Amagat's experiments on the compressibility of ethylene enable us to calculate the correction due to deviation from Boyle's Law. Since, however, the lowest pressure used by Amagat was 30 atmospheres, the correction term must be put in a slightly different form. Using Van der Waals' equation

$$(p + a/v^2)(v - b) = Rt$$

to express the relation between $p$, $v$, and $t$, it is easily shown that the correction term takes the form $1 + a/pv^2 - b/v$.

Baynes has calculated Van der Waals' constants from Amagat's observations, and finds (Nature, vol. 22, p. 186) $a = .00786$, $b = .0024$. Hence since in my experiments $p = 1$ and $v = 288/273$, we get the correction 1.007.

Two determinations of the velocity of sound at atmospheric pressure gave the following results, the theoretical value of the density of the gas being used in the calculation of $\gamma$.

Table XIV.

<table>
<thead>
<tr>
<th>$t$</th>
<th>$l$</th>
<th>$v$</th>
<th>$\rho$</th>
<th>$1 + \frac{1}{p}\frac{d}{dt}v^2$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-4</td>
<td>46.32</td>
<td>48.51</td>
<td>.9075</td>
<td>1.007</td>
<td>1.251</td>
<td>1.249</td>
</tr>
<tr>
<td>15</td>
<td>46.32</td>
<td>48.54</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>Mean</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>1.250</td>
<td>1.740</td>
</tr>
</tbody>
</table>

§ 8. Vinyl Bromide (C₂H₃Br).

The material was made by gently warming ethylene dibromide with alcoholic potash. The issuing gas was condensed, fractionated, allowed to stand over calcium chloride, and again fractionated.

Four weighed tubes to contain the liquid for vapour-density determinations were filled in a freezing mixture, but on coming to the temperature of the room two burst, so that only two were left for use. These gave the following results:—
DR. J. W. CAPSTICK ON THE RATIO OF THE

Table XV.

<table>
<thead>
<tr>
<th>p</th>
<th>t</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>311</td>
<td>15.2</td>
<td>3.677</td>
</tr>
<tr>
<td>436</td>
<td>15</td>
<td>3.700</td>
</tr>
</tbody>
</table>

Since two observations are not sufficient to give the curve, a set of relative density determinations was made in the usual way. The results are shown in Table XIV.

Table XVI.

<table>
<thead>
<tr>
<th>p</th>
<th>v</th>
<th>pv</th>
</tr>
</thead>
<tbody>
<tr>
<td>155.35</td>
<td>12.415</td>
<td>1928</td>
</tr>
<tr>
<td>220.6</td>
<td>8.68</td>
<td>1915</td>
</tr>
<tr>
<td>250.3</td>
<td>7.627</td>
<td>1914</td>
</tr>
<tr>
<td>305.35</td>
<td>6.224</td>
<td>1901</td>
</tr>
<tr>
<td>503</td>
<td>3.721</td>
<td>1872</td>
</tr>
</tbody>
</table>

The reciprocals of the numbers in the third column are proportional to the specific gravity of the vapour. These reciprocals with the scale suitably altered so as to coincide as nearly as possible with the values in Table XV. are marked by circles on the curve of fig. 5. The two values of the absolute density are marked by crosses.

The curve was employed in the usual way for finding the numbers in the fifth and sixth columns of Table XVII.

Fig. 5.
Table XVII.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$l$</th>
<th>$T$</th>
<th>$\rho$</th>
<th>$1 + \frac{1 d}{\rho d^2 \rho v}$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>15</td>
<td>22.98</td>
<td>48.53</td>
<td>3.890</td>
<td>1.026</td>
<td>1.185</td>
<td>2.770</td>
</tr>
<tr>
<td>430</td>
<td>15.6</td>
<td>22.97</td>
<td>48.63</td>
<td>3.705</td>
<td>1.026</td>
<td>1.183</td>
<td>2.808</td>
</tr>
<tr>
<td>560</td>
<td>15.2</td>
<td>22.91</td>
<td>48.54</td>
<td>3.749</td>
<td>1.027</td>
<td>1.207</td>
<td>2.566</td>
</tr>
</tbody>
</table>

Mean . 1.198 2.715

§ 9. Allyl Chloride ($\text{C}_3\text{H}_5\text{Cl}$).

Table XVIII.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$l$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>14.2</td>
<td>2.655</td>
</tr>
<tr>
<td>116</td>
<td>13.2</td>
<td>2.660</td>
</tr>
<tr>
<td>128</td>
<td>12.8</td>
<td>2.659</td>
</tr>
<tr>
<td>152</td>
<td>12.6</td>
<td>2.664</td>
</tr>
<tr>
<td>184</td>
<td>15.0</td>
<td>2.667</td>
</tr>
</tbody>
</table>

Fig. 6.

Table XIX.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$l$</th>
<th>$T$</th>
<th>$\rho$</th>
<th>$1 + \frac{1 d}{\rho d^2 \rho v}$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>13.5</td>
<td>26.58</td>
<td>48.42</td>
<td>2.658</td>
<td>1.006</td>
<td>1.134</td>
<td>4.090</td>
</tr>
<tr>
<td>142</td>
<td>13.2</td>
<td>26.56</td>
<td>48.40</td>
<td>2.662</td>
<td>1.008</td>
<td>1.137</td>
<td>4.016</td>
</tr>
<tr>
<td>147</td>
<td>13.6</td>
<td>26.53</td>
<td>48.43</td>
<td>2.663</td>
<td>1.008</td>
<td>1.134</td>
<td>4.128</td>
</tr>
<tr>
<td>156</td>
<td>14.7</td>
<td>26.65</td>
<td>48.52</td>
<td>2.665</td>
<td>1.009</td>
<td>1.142</td>
<td>3.859</td>
</tr>
</tbody>
</table>

Mean . 1.137 4.023

4 E 2
§ 10. **Allyl Bromide (C₃H₅Br).**

### Table XX.

<table>
<thead>
<tr>
<th>( p )</th>
<th>( t )</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>13-4</td>
<td>4-174</td>
</tr>
<tr>
<td>74</td>
<td>14-9</td>
<td>4-187</td>
</tr>
<tr>
<td>70</td>
<td>16-4</td>
<td>4-184</td>
</tr>
<tr>
<td>68</td>
<td>16-2</td>
<td>4-188</td>
</tr>
</tbody>
</table>

---

**Fig. 7.**

---

### Table XXI.

<table>
<thead>
<tr>
<th>( p )</th>
<th>( t_1 )</th>
<th>( t_2 )</th>
<th>( \ell )</th>
<th>( l' )</th>
<th>( \rho )</th>
<th>( 1 + \frac{1}{p} \frac{d}{dv} \rho )</th>
<th>( \gamma )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>15-8</td>
<td>21-20</td>
<td>48-57</td>
<td>4-195</td>
<td>1-013</td>
<td>1-149</td>
<td>3-704</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>15-5</td>
<td>21-28</td>
<td>48-59</td>
<td>4-194</td>
<td>1-013</td>
<td>1-147</td>
<td>3-708</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>15-5</td>
<td>21-25</td>
<td>48-58</td>
<td>4-189</td>
<td>1-011</td>
<td>1-141</td>
<td>3-929</td>
<td></td>
</tr>
</tbody>
</table>

Mean . . | 1-145 | 3-800 |

---

§ 11. **Carbon Dioxide (CO₂).**

The gas was prepared from marble and hydrochloric acid. It was purified by being washed with water and passed over bicarbonate of potash and calcium chloride.

Regnault's value, 1-529, was taken as the specific gravity of the gas.

The experiments of Andrews afford material for calculating the term \( 1 + \frac{1}{p} \frac{d}{dv} \rho \). Using the results as tabulated by Landolt and Börrnstein (2nd edition, p. 83), the term has the value 1-007 for atmospheric pressure and temperatures between 0° and 30°.

The following table gives the results of the experiments, the pressure of the gas being in each case that of the atmosphere.
SPECIFIC HEATS OF SOME COMPOUND GASES.

Table XXII.

<table>
<thead>
<tr>
<th>t.</th>
<th>l.</th>
<th>v.</th>
<th>p.</th>
<th>$1 + \frac{1}{p} \frac{d}{dv}$</th>
<th>γ</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.2</td>
<td>37.92</td>
<td>48.84</td>
<td>1.529</td>
<td>1.007</td>
<td>1.306</td>
<td></td>
</tr>
<tr>
<td>18.1</td>
<td>37.97</td>
<td>48.83</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>1.311</td>
</tr>
<tr>
<td>17.4</td>
<td>37.92</td>
<td>48.75</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>1.312</td>
</tr>
<tr>
<td>14.7</td>
<td>37.65</td>
<td>48.53</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>1.304</td>
</tr>
<tr>
<td>11.9</td>
<td>37.48</td>
<td>48.28</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>1.306</td>
</tr>
<tr>
<td>12.6</td>
<td>37.57</td>
<td>48.34</td>
<td>..</td>
<td>..</td>
<td>..</td>
<td>1.310</td>
</tr>
</tbody>
</table>

Mean                           1.308 1.224

Previous determinations of the ratio of the specific heats of carbon dioxide have given the following results:

<table>
<thead>
<tr>
<th>t.</th>
<th>γ</th>
<th>Observer</th>
</tr>
</thead>
<tbody>
<tr>
<td>19°</td>
<td>1.291</td>
<td>CAZIN ('Ann. de Chim.,' 56, 206)</td>
</tr>
<tr>
<td>0</td>
<td>1.311</td>
<td>DE LUCCHI ('Nuov. Cim.,' 11, 11)</td>
</tr>
<tr>
<td>100</td>
<td>1.282</td>
<td>WÜLLNER ('Wied. Ann.,' 4, 321)</td>
</tr>
<tr>
<td>9-34</td>
<td>1.285</td>
<td>MÜLLER ('Wied. Ann.,' 18, 94)</td>
</tr>
<tr>
<td></td>
<td>1.29</td>
<td>JAMIN and RICHARD ('Comptes Rendus,' 71, 336)</td>
</tr>
</tbody>
</table>

All these observers have used the equations of a perfect gas. My own result would be 1.299 without the correction for deviation from BOYLE'S LAW.

§ 12. Carbon Bisulphide (CS₂).

The liquid was first distilled from lime over which it had stood several days. It was then shaken repeatedly with mercury, dried with calcium chloride, and redistilled.

As the determinations of the absolute vapour density give an unsatisfactory curve, two of the experiments giving values rather more than a tenth per cent. away from the curve through the other three, a separate experiment was made to find the relative densities in the usual way. The results of this experiment are shown in Table XXIII, and fig. 8.

Table XXIII.

<table>
<thead>
<tr>
<th>T.</th>
<th>p.</th>
<th>v.</th>
<th>pv/T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>286.7</td>
<td>123.3</td>
<td>118.6</td>
<td>49.56</td>
</tr>
<tr>
<td>170</td>
<td>85.8</td>
<td>85.8</td>
<td>49.45</td>
</tr>
<tr>
<td>197.9</td>
<td>73.6</td>
<td>73.6</td>
<td>49.38</td>
</tr>
</tbody>
</table>
Table XXIV. gives the results of the vapour-density determinations. The numbers in the fourth column are taken from the curve in fig. 8, and when multiplied by the corresponding numbers in the third column should give a constant, if the two series of experiments are consistent. The products are shown in the last column.

**Table XXIV.**

<table>
<thead>
<tr>
<th>( p )</th>
<th>( t )</th>
<th>( \rho )</th>
<th>( p\rho/T )</th>
<th>( p\rho\rho/T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>134</td>
<td>11-4</td>
<td>2\cdot647</td>
<td>49\cdot53</td>
<td>1311</td>
</tr>
<tr>
<td>147</td>
<td>11\cdot6</td>
<td>2\cdot644</td>
<td>49\cdot50</td>
<td>1309</td>
</tr>
<tr>
<td>123</td>
<td>11\cdot6</td>
<td>2\cdot654</td>
<td>49\cdot30</td>
<td>1310</td>
</tr>
<tr>
<td>125</td>
<td>12\cdot4</td>
<td>2\cdot643</td>
<td>49\cdot56</td>
<td>1310</td>
</tr>
<tr>
<td>161</td>
<td>9\cdot8</td>
<td>2\cdot648</td>
<td>49\cdot47</td>
<td>1310</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td></td>
<td></td>
<td></td>
<td>1310</td>
</tr>
</tbody>
</table>

The mean of the numbers in the last column of this table divided by the ordinate of the curve in fig. 8 for a given pressure, gives the best value of the vapour-density for that pressure. The fifth column of the table below was calculated in this way.

**Table XXV.**

<table>
<thead>
<tr>
<th>( p )</th>
<th>( t )</th>
<th>( \gamma )</th>
<th>( \beta )</th>
<th>( 1 + \frac{1}{\rho} \frac{d \rho}{d\gamma} )</th>
<th>( \eta )</th>
<th>( \gamma )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td>11\cdot4</td>
<td>27\cdot71</td>
<td>48\cdot23</td>
<td>2\cdot643</td>
<td>1\cdot006</td>
<td>1\cdot236</td>
<td>1\cdot890</td>
</tr>
<tr>
<td>130</td>
<td>16</td>
<td>27\cdot94</td>
<td>48\cdot63</td>
<td>2\cdot644</td>
<td>1\cdot006</td>
<td>1\cdot236</td>
<td>1\cdot890</td>
</tr>
<tr>
<td>141</td>
<td>12\cdot8</td>
<td>27\cdot77</td>
<td>48\cdot24</td>
<td>2\cdot645</td>
<td>1\cdot007</td>
<td>1\cdot243</td>
<td>1\cdot819</td>
</tr>
<tr>
<td>150</td>
<td>13\cdot4</td>
<td>27\cdot79</td>
<td>48\cdot42</td>
<td>2\cdot647</td>
<td>1\cdot008</td>
<td>1\cdot237</td>
<td>1\cdot903</td>
</tr>
<tr>
<td>156</td>
<td>14</td>
<td>27\cdot86</td>
<td>48\cdot46</td>
<td>2\cdot648</td>
<td>1\cdot008</td>
<td>1\cdot242</td>
<td>1\cdot843</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1\cdot239</td>
<td></td>
<td>1\cdot869</td>
</tr>
</tbody>
</table>

The gas was prepared by warming antimony sulphide with hydrochloric acid. It was washed with water, and dried by being passed over calcium chloride.

An experiment to determine the deviation of the gas from Boyle's Law gave the following result:

<table>
<thead>
<tr>
<th>T.</th>
<th>v.</th>
<th>p.</th>
<th>pv/T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>291.8</td>
<td>38.67</td>
<td>967.8</td>
<td>128.2</td>
</tr>
<tr>
<td>49.8</td>
<td>754.65</td>
<td>128.7</td>
<td></td>
</tr>
<tr>
<td>64.07</td>
<td>587.85</td>
<td>129.0</td>
<td></td>
</tr>
<tr>
<td>55.12</td>
<td>443.05</td>
<td>129.2</td>
<td></td>
</tr>
<tr>
<td>102.2</td>
<td>369.5</td>
<td>129.4</td>
<td></td>
</tr>
</tbody>
</table>

These numbers give 0.011 as the value of \( \frac{1}{p} \frac{d}{dv} pv \) at 760 millims.

The theoretical density 1.177 is used in the calculation of \( \gamma \).

Three determinations of the velocity of sound at atmospheric pressure give the following results:

<table>
<thead>
<tr>
<th>t.</th>
<th>l.</th>
<th>v.</th>
<th>p.</th>
<th>( 1 + \frac{1}{p} \frac{d}{dv} pv ).</th>
<th>( \gamma )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.8</td>
<td>43.31</td>
<td>48.78</td>
<td>1.177</td>
<td>1.011</td>
<td>1.321</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>43.46</td>
<td>48.85</td>
<td>..</td>
<td>..</td>
<td>1.322</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>43.42</td>
<td>48.83</td>
<td>..</td>
<td>..</td>
<td>1.321</td>
<td></td>
</tr>
</tbody>
</table>

Mean . | . | 1.321 | 1.165 |

§ 14. Ethyl Formate (HCOOC₃H₅).

The ethyl formate used in the experiments was allowed to stand over anhydrous carbonate of potash and calcium chloride, and was then fractionated. This treatment made the boiling-point steady, but the substance is so readily decomposed, that the operation had to be repeated at times, and consequently the material used was not the same in all the experiments.

Every precaution was taken to keep the apparatus thoroughly dry inside and so prevent decomposition; but in spite of this the vapour-density results were not concordant enough to give a trustworthy curve. Hence it was necessary to make a determination of the relative densities.
The tables and figures have exactly the same meaning as the corresponding ones for carbon bisulphide. Table XXVIII. and fig. 9 exhibit the results of the relative density determination, Table XXIX. those of the absolute determinations, and Table XXX. gives the values found for $\gamma$ and $\beta$.

### Table XXVIII.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$\frac{p^o}{t + 273}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>92</td>
<td>17'9</td>
<td>25'67</td>
</tr>
<tr>
<td>105</td>
<td>..</td>
<td>25'62</td>
</tr>
<tr>
<td>119</td>
<td>..</td>
<td>25'55</td>
</tr>
<tr>
<td>134</td>
<td>..</td>
<td>25'52</td>
</tr>
<tr>
<td>148</td>
<td>..</td>
<td>25'46</td>
</tr>
</tbody>
</table>

### Table XXIX.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$p_r$</th>
<th>$\frac{p_r}{t + 273}$</th>
<th>$\frac{p_{eq}}{t + 273}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>18</td>
<td>2'487</td>
<td>25'61</td>
<td>6368</td>
</tr>
<tr>
<td>109</td>
<td>17'8</td>
<td>2'489</td>
<td>25'59</td>
<td>6369</td>
</tr>
<tr>
<td>110</td>
<td>18'4</td>
<td>2'485</td>
<td>25'59</td>
<td>6359</td>
</tr>
<tr>
<td>131</td>
<td>18'2</td>
<td>2'498</td>
<td>25'52</td>
<td>6372</td>
</tr>
<tr>
<td>131</td>
<td>18'3</td>
<td>2'499</td>
<td>25'52</td>
<td>6377</td>
</tr>
<tr>
<td>149</td>
<td>18'6</td>
<td>2'498</td>
<td>25'45</td>
<td>6357</td>
</tr>
</tbody>
</table>

Mean .................................. 6367
### Table XXX.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t'$</th>
<th>$l'$</th>
<th>$t$</th>
<th>$l$</th>
<th>$l'$</th>
<th>$1+\frac{1}{d} \frac{d}{dp} \frac{1}{d}$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>20.8</td>
<td>27.67</td>
<td>49.03</td>
<td>2.482</td>
<td>1.014</td>
<td>1.129</td>
<td>4.450</td>
<td></td>
</tr>
<tr>
<td>99</td>
<td>18.9</td>
<td>27.49</td>
<td>48.86</td>
<td>2.485</td>
<td>1.015</td>
<td>1.124</td>
<td>4.694</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>19.9</td>
<td>27.49</td>
<td>48.96</td>
<td>2.486</td>
<td>1.015</td>
<td>1.120</td>
<td>4.883</td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>20.8</td>
<td>27.57</td>
<td>49.05</td>
<td>2.492</td>
<td>1.018</td>
<td>1.128</td>
<td>4.578</td>
<td></td>
</tr>
<tr>
<td>141</td>
<td>20.4</td>
<td>27.43</td>
<td>48.97</td>
<td>2.500</td>
<td>1.021</td>
<td>1.128</td>
<td>4.640</td>
<td></td>
</tr>
<tr>
<td>142</td>
<td>19.4</td>
<td>27.42</td>
<td>48.92</td>
<td>2.500</td>
<td>1.021</td>
<td>1.128</td>
<td>4.597</td>
<td></td>
</tr>
</tbody>
</table>

Mean ... | 1.125 | 4.640 |

§ 15. Methyl Acetate (CH₃COOCH₃).

Methyl acetate proved to be more troublesome than any of the other substances investigated, and it is with some hesitation that I venture to publish the results of my experiments on it. Time after time the liquid was shaken with calcium chloride and fractionated, but the boiling-point was never as steady as could be wished. One of the decomposition products is methyl alcohol, which has nearly the same boiling-point as methyl acetate itself, and cannot be removed by fractionation, so that it is hardly to be hoped that the final product was quite pure.

The experiments with the Kundt apparatus, given below in Table XXXI., are not the only ones that were made. After each purification several experiments were made, and it was found that the wave-length of sound in the vapour gradually diminished—presumably in consequence of the gradual removal of methyl alcohol. The set given below were made on the particular sample that gave the shortest wave-length.

If the vapour-density determinations gave the true density of the material used in the velocity of sound experiments, a little impurity would have scarcely any effect on $\gamma$, but the vapour-density observations are specially liable to error. The quantity of methyl acetate used in an experiment is small—not more than a quarter of a gramme—and a very little moisture on the glass may bring about the decomposition of quite an appreciable percentage of the vapour. It is probably for this reason that the experimental error of the vapour-density observations is greater than usual, the divergence from the mean reaching 1 part in 400.

The tabulation of the results is the same as before. Table XXXI. and fig. 10 give the relative density determinations. Table XXXII. gives the absolute density results, and Table XXXIII. gives the values found for $\gamma$. 

MDCCCXCV.—A. 4 F
Table XXXI.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$\frac{p}{t + 273}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>18.9</td>
<td>33.58</td>
</tr>
<tr>
<td>105</td>
<td>...</td>
<td>33.38</td>
</tr>
<tr>
<td>117</td>
<td>...</td>
<td>33.35</td>
</tr>
<tr>
<td>127</td>
<td>...</td>
<td>33.28</td>
</tr>
<tr>
<td>137</td>
<td>...</td>
<td>33.20</td>
</tr>
<tr>
<td>153</td>
<td>...</td>
<td>33.00</td>
</tr>
</tbody>
</table>

Fig. 10.

Table XXXII.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$t$</th>
<th>$\rho$</th>
<th>$\frac{p}{t + 273}$</th>
<th>$\frac{p\rho}{t + 273}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>18.6</td>
<td>2.483</td>
<td>33.72</td>
<td>8317</td>
</tr>
<tr>
<td>71</td>
<td>18.1</td>
<td>2.488</td>
<td>33.68</td>
<td>8319</td>
</tr>
<tr>
<td>82</td>
<td>18.8</td>
<td>2.486</td>
<td>33.62</td>
<td>8360</td>
</tr>
<tr>
<td>87</td>
<td>17.4</td>
<td>2.485</td>
<td>33.57</td>
<td>8343</td>
</tr>
<tr>
<td>92</td>
<td>17.6</td>
<td>2.488</td>
<td>33.53</td>
<td>8375</td>
</tr>
<tr>
<td>97</td>
<td>18</td>
<td>2.491</td>
<td>33.50</td>
<td>8345</td>
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<tr>
<td>100</td>
<td>17.7</td>
<td>2.506</td>
<td>33.47</td>
<td>8355</td>
</tr>
<tr>
<td>109</td>
<td>16.8</td>
<td>2.503</td>
<td>33.47</td>
<td>8375</td>
</tr>
<tr>
<td>102</td>
<td>16.6</td>
<td>2.500</td>
<td>33.46</td>
<td>8364</td>
</tr>
<tr>
<td>114</td>
<td>18.4</td>
<td>2.509</td>
<td>33.37</td>
<td>8360</td>
</tr>
</tbody>
</table>

Mean ... 8366
SPECIFIC HEATS OF SOME COMPOUND GASES.

Table XXXIII.

<table>
<thead>
<tr>
<th>p.</th>
<th>l.</th>
<th>l.</th>
<th>r.</th>
<th>p.</th>
<th>(1 + \frac{1}{p} \frac{d}{dc} \rho_c)</th>
<th>q.</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>18.2</td>
<td>27.51</td>
<td>48.82</td>
<td>2.496</td>
<td>1.019</td>
<td>1.137</td>
<td>4.234</td>
</tr>
<tr>
<td>102</td>
<td>19.7</td>
<td>27.57</td>
<td>48.96</td>
<td>2.501</td>
<td>1.020</td>
<td>1.139</td>
<td>4.172</td>
</tr>
<tr>
<td>103</td>
<td>19.8</td>
<td>27.51</td>
<td>48.97</td>
<td>2.502</td>
<td>1.020</td>
<td>1.134</td>
<td>4.365</td>
</tr>
<tr>
<td>104</td>
<td>19.3</td>
<td>27.48</td>
<td>48.84</td>
<td>2.502</td>
<td>1.021</td>
<td>1.139</td>
<td>4.194</td>
</tr>
<tr>
<td>86</td>
<td>9.05</td>
<td>27.10</td>
<td>48.03</td>
<td>2.492</td>
<td>1.018</td>
<td>1.137</td>
<td>4.212</td>
</tr>
</tbody>
</table>

Mean... 1.137  4.235

§ 16. Silicon Tetrachloride (SiCl₄).

Silicon tetrachloride is much more unstable even than the two substances last described. It decomposes so readily in the presence of moisture that white fumes of silica are given off if the bottle containing the liquid is left open.

The Kundt apparatus was easily dried, so there was probably no appreciable decomposition in the velocity of sound experiments, but the vapour-density apparatus was more difficult to keep from contact with moist air, and at the end of the set of experiments a slight dimming of the glass from the deposit of silica showed that the attempt to keep out moisture had not been entirely successful.

Table XXXIV.

<table>
<thead>
<tr>
<th>p.</th>
<th>l.</th>
<th>(\rho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>14</td>
<td>5.797</td>
</tr>
<tr>
<td>88</td>
<td>14.1</td>
<td>5.810</td>
</tr>
<tr>
<td>106</td>
<td>14.1</td>
<td>5.848</td>
</tr>
<tr>
<td>110</td>
<td>13.6</td>
<td>5.875</td>
</tr>
<tr>
<td>126</td>
<td>16</td>
<td>5.879</td>
</tr>
<tr>
<td>138</td>
<td>16.1</td>
<td>5.878</td>
</tr>
</tbody>
</table>

Fig. 11.
§ 17. Discussion of the Results.

As many of the above gases are closely related to those included in my former paper, the whole of the results of the two series are included in one table.

Table XXXVI.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>( v )</th>
<th>( \beta )</th>
<th>( \beta + \frac{1}{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>1.313</td>
<td>1.129</td>
<td>226</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>CH₃Cl</td>
<td>1.279</td>
<td>1.506</td>
<td>301</td>
</tr>
<tr>
<td>Methyl bromide</td>
<td>CH₃Br</td>
<td>1.274</td>
<td>1.573</td>
<td>314</td>
</tr>
<tr>
<td>Methyl iodide</td>
<td>CH₃I</td>
<td>1.286</td>
<td>1.597</td>
<td>319</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>CH₂CH₂</td>
<td>1.219</td>
<td>2.175</td>
<td>435</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>1.154</td>
<td>3.065</td>
<td>701</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl₄</td>
<td>1.130</td>
<td>4.411</td>
<td>882</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>1.182</td>
<td>2.659</td>
<td>332</td>
</tr>
<tr>
<td>Ethyl chloride</td>
<td>CH₃Cl</td>
<td>1.187</td>
<td>2.838</td>
<td>355</td>
</tr>
<tr>
<td>Ethyl bromide</td>
<td>CH₃Br</td>
<td>1.188</td>
<td>2.809</td>
<td>351</td>
</tr>
<tr>
<td>Ethylene chloride</td>
<td>CH₂CH₂Cl</td>
<td>1.137</td>
<td>4.184</td>
<td>523</td>
</tr>
<tr>
<td>Ethylidene chloride</td>
<td>CH₃CH₂Cl</td>
<td>1.134</td>
<td>4.243</td>
<td>533</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₆</td>
<td>1.139</td>
<td>4.427</td>
<td>402</td>
</tr>
<tr>
<td>Normal propyl chloride</td>
<td>C₃H₇Cl</td>
<td>1.126</td>
<td>4.403</td>
<td>408</td>
</tr>
<tr>
<td>Isopropyl chloride</td>
<td>C₃H₇Cl</td>
<td>1.127</td>
<td>4.465</td>
<td>406</td>
</tr>
<tr>
<td>Isopropyl bromide</td>
<td>C₃H₇Br</td>
<td>1.131</td>
<td>4.415</td>
<td>401</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C₂H₄</td>
<td>1.250</td>
<td>1.740</td>
<td>290</td>
</tr>
<tr>
<td>Vinyl bromide</td>
<td>C₃H₇Br</td>
<td>1.198</td>
<td>2.715</td>
<td>452</td>
</tr>
<tr>
<td>Allyl chloride</td>
<td>C₃H₇Cl</td>
<td>1.137</td>
<td>4.023</td>
<td>447</td>
</tr>
<tr>
<td>Allyl bromide</td>
<td>C₃H₇Br</td>
<td>1.145</td>
<td>3.860</td>
<td>422</td>
</tr>
<tr>
<td>Ethyl formate</td>
<td>H₂C₂O₂CH₃</td>
<td>1.124</td>
<td>4.640</td>
<td>422</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>CH₃COOCH₃</td>
<td>1.137</td>
<td>4.255</td>
<td>388</td>
</tr>
<tr>
<td>Sulphuretted hydrogen</td>
<td>SH₂</td>
<td>1.321</td>
<td>1.165</td>
<td>388</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>1.305</td>
<td>1.224</td>
<td>408</td>
</tr>
<tr>
<td>Carbon bisulphide</td>
<td>CS₂</td>
<td>1.239</td>
<td>1.869</td>
<td>623</td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td>SiCl₄</td>
<td>1.129</td>
<td>4.585</td>
<td>917</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>1.129</td>
<td>4.585</td>
<td></td>
</tr>
</tbody>
</table>
My former conclusion that monohalogen derivatives of the same paraffin have the same $\gamma$ can now be stated in more general terms. The two allyl compounds show that it is not restricted to saturated hydrocarbons, and the equality of $\gamma$ of ethylene and ethylidene chlorides extends it to isomeric dihalogen derivatives. Hence, so far as the experiments have gone, we can say that without any exception corresponding halogen derivatives of the same hydrocarbon have the same ratio of the specific heats.

Similarly it appears that the equality of $\gamma$ for the two propyl chlorides is not an isolated fact, for two other pairs of isomeric bodies, viz., ethylene and ethylidene chlorides and methyl acetate and ethyl formate prove to have the same $\gamma$. As I have mentioned above, there is some doubt about the results for the two last mentioned, but at present the balance of evidence is in favour of the statement that isomeric compounds have the same $\gamma$.

In the case of the paraffins ethane and propane, it was shown in my former paper that one H can be replaced by a halogen without altering the value of $\gamma$, but that the introduction of a halogen into methane causes a fall in $\gamma$. We see now that the unsaturated gas ethylene behaves in the same way as methane, for the $\gamma$ of vinyl bromide is markedly lower than that of ethylene. Thus the possibility of interchange of hydrogen with a halogen without altering $\gamma$ is not general, a fact that is brought out still more clearly by a consideration of the higher substitution products.

It was shown by Strecker* that hydrochloric, hydrobromic and hydroiodic acids all have nearly the same $\gamma$ as hydrogen, namely 1 4, whilst the $\gamma$'s of chlorine, bromine, iodine and iodine chloride all lie near 1 3. Hence in this case one halogen can be put in the place of hydrogen without affecting $\gamma$, but the introduction of a second halogen causes a large fall.

The paraffin derivatives show the same feature. The second Cl introduced into the molecule invariably causes a large fall in $\gamma$ whether the first has done so or not. Thus, whilst ethyl chloride has the same $\gamma$ as ethane, ethylene and ethylidene chlorides are 4 per cent. lower.

The methane substitution products are volatile enough to allow the whole series to be investigated, and here we find that every successive chlorine atom introduced causes a fall in $\gamma$.

The work done on the last four gases in the table is only the beginning of a line of investigation, the completion of which would require an entire remodelling of my apparatus, so as to enable it to stand higher temperatures. The object of the experiments was to find whether other chemically analogous atoms are interchangeable in the same way as the halogens.

Although C and Si replace each other in many compounds, CCl$_4$ and SiCl$_4$ are not strictly analogous, for they violate the usual rule that the compound with the higher molecular weight has the higher boiling-point. They appear however to have the same $\gamma$.

The further investigation of the relations of carbon and silicon would be a matter of some difficulty, from the readiness with which the silicon compounds are decomposed.

Corresponding oxygen and sulphur compounds are numerous and stable, but most of the sulphur compounds have too high boiling-points to give a sufficiently dense vapour at the atmospheric pressure.

The value of $\gamma$ for sulphuretted hydrogen was got for comparison with that found by other observers of water. Experiments made on water vapour have given the following results:

<table>
<thead>
<tr>
<th>$t$, $\gamma$</th>
<th>Observer</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>1.274</td>
</tr>
<tr>
<td>94</td>
<td>1.33</td>
</tr>
<tr>
<td>100</td>
<td>1.321</td>
</tr>
<tr>
<td>103</td>
<td>1.277</td>
</tr>
<tr>
<td>144-300</td>
<td>1.287</td>
</tr>
</tbody>
</table>

These are very discordant, but some of them seem to be of doubtful validity. Bömmel made only a single experiment, and measured only three dust figures. De Lucchi used Clément and Desormes' method, with a receiver so small that, in the light of Röntgen's experiments, his result is probably too low. Neyreneuf and Cohen both assumed that the vapour obeys Boyle's Law, the latter observer trusting to superheating of the gas to justify the assumption. Jäger alone carried out his calculations in a manner that seems allowable, and his result is almost the same as I have found for sulphuretted hydrogen.

The two gases CO$_2$ and CS$_2$ have widely different values of the ratio of the specific heats, so that the possibility of interchange of O and S without altering $\gamma$ does not at least extend to two atoms.

It is worth noticing that according to Regnault's results the molecular heat at constant pressure is nearly the same for the members of any one of the groups—H$_2$S and H$_2$O; (C$_2$H$_5$)$_2$S and (C$_2$H$_5$)$_2$O; SiCl$_4$, SnCl$_4$, and TiCl$_4$; so that it seems likely that the laws I have found to hold for the halogens will prove to hold for other groups of analogous elements.

Up to this point, only the relations of the $\gamma$'s of the gases to each other have been discussed, though it is from their enabling us to calculate $\beta$ that the values of $\gamma$ are likely to prove ultimately most useful.

If two gases have the same $\gamma$, they have approximately the same $\beta$, that is, for a small rise of temperature the quantity of energy absorbed by the internal vibrations of the molecules bears the same ratio to the increase of kinetic energy of translation of the whole molecule in the two cases.
Thus, for instance, the molecules CH₃Cl, CH₃Br and CH₃I have the same energy absorbing power, from which it follows, with a high degree of probability, that the halogen atoms in these molecules, in spite of their great difference in mass, absorb the same share of the total energy. It is very improbable that if they did not, the redistribution of energy in the molecule on interchange of the halogens would result in the total capacity being unchanged. Similarly, we may infer from the behaviour of hydrogen, ethane, and propane that the chlorine atom may in some cases have the same energy absorbing power as the hydrogen it replaces.

An instance of another kind of interchange that can be made without disturbing the distribution of energy, is seen in the case of the two propyl chlorides and the two dichlorethanes. Trusting to graphic formulæ the chemist explains the difference between the two members of a pair as being due to a hydrogen changing places with a chlorine within the molecule, the configuration being in other respects unchanged.

The relation of methyl acetate to ethyl formate is explained in a somewhat similar way, for if we write the formula of ethyl formate in the form CH₃—CH₂—O—CO—H—we can convert it into that of methyl acetate by interchanging CH₃ and CO. Thus it appears that, if we can trust graphic formulæ to give information of this kind, groups may be interchanged without disturbing $\beta$. It would be of interest to carry out this point farther, and find whether one of the groups could be removed from the molecule, and the other put in its place without altering $\beta$. Has, for instance, methyl-ethyl oxide, which would be obtained by replacing CO in either of the above by CH₂, the same $\gamma$? It is probable that valuable information on the status of the radicle might be got by the determination of $\beta$ for a number of suitably chosen compounds.

It appears then that a single atom of hydrogen, oxygen or carbon can in many cases be replaced by chlorine, sulphur and silicon respectively, without disturbing the distribution of energy in the molecule, but in no case investigated can the replacement be repeated without bringing about a large increase in $\beta$. Hence we conclude that an atom has not an intrinsic heat capacity which it carries with it unchanged into any gaseous molecule of which it forms part, but that it is affected by its neighbours. In other words $\beta$ is not an additive quantity, for the configuration of the molecule plays a part in the distribution of energy.

My experiments would not be inconsistent with the supposition that the configuration is the sole feature that fixes the distribution, but until more definite evidence is obtained—especially with regard to the physical significance of radicles—this must remain no more than a suggestion.

It was pointed out many years ago by Naumann, when experimental evidence was scanty, that $\beta$ divided by the number of atoms in the molecule was nearly equal to $\cdot 33$. If this held generally, it would be an important fact, for it would point to something of the nature of Boltzmann's Theorem being true, and as the statement is sometimes quoted by writers, I have given the quotients in question in the fifth
column of Table XXXVI. It will be seen that in many cases $\beta/n$ shows a rough approximation to 0.33, but no more. Even allowing for the exaggeration of the experimental error by the nature of the equation connecting $\beta$ and $\gamma$, it cannot be said that the intramolecular energy is proportional to the number of atoms in the molecule. The paraffins themselves and their monohalogen derivatives show the closest approximation, but even in their case the quotient appears to increase as $n$ increases.

This last fact and the extract below from an article by Professor J. J. Thomson (Watts, 'Dictionary of Chemistry,' vol. 1, p. 89), suggest another relation among the $\beta$'s that looks more promising. The extract in question is as follows:—“Though there is strong evidence against the truth of the theorem (i.e., Boltzmann's Theorem) in this form, and the mathematical proof of it is unsatisfactory, yet a very special case of it is probably true, viz., that if we have a molecule consisting of $n$ atoms approximately symmetrically arranged (that is, if the distance between a particular pair of atoms is not always very much less than the distances between the other pairs), then the ratio of the mean total kinetic energy of the molecule to the energy due to the translatory motion of the centre of gravity is proportional to $n$, the number of atoms in the molecule.”

If then the molecules of the gases I have investigated are symmetrical in the above sense, we ought to find $(\beta + 1)/n$ constant. Looking down the last column of the table it will be seen that, though this is by no means the case throughout, yet if we confine ourselves to the paraffins and their derivatives that have not more than one halogen atom in the molecule, there is a very striking agreement.

The mean of the eleven quotients so defined is 0.493. Methane, as we have already seen, falls out of the series, and here it diverges to the extent of 18 per cent., which is equivalent to a divergence of about 3 per cent. in $\gamma$. The $\gamma$ of ethane would have to be about 1 per cent. lower to give complete agreement. In the case of all the rest the divergence is well within the probable experimental error.
XVI. Iron and Steel at Welding Temperatures.

By T. Wrightson, M.P., Memb. Inst. C.E.

Communicated by Professor Roberts-Austen, C.B., F.R.S.

Received February 2,—Read February 21, 1895.

In 1879-80 I drew attention to a method of measuring the changes of volume taking place in cast iron while passing through the varying temperatures lying between its cold and its molten state.

If a ball of cast iron at atmospheric temperature be immersed in a vessel of molten iron of the same quality, it first sinks. In a few seconds it comes to the surface, owing to the heat penetrating and expanding the ball, which, causing increased displacement of the fluid metal, produces the increased buoyancy observed.

The increase of buoyancy does not stop here, as the ball continues to rise above the surface of the fluid metal to a considerable height, until it arrives at the melting point, when it rapidly melts down and joins the molten iron in the vessel.

An instrument was designed by me* to measure this change in the volume of iron. The principle of the instrument is based on the law of flotation of bodies in liquids, by which an increase of buoyancy in a submerged body is equivalent to an increase in weight of the displaced fluid.

The ball of cast iron to be experimented upon is hung by a chain and rods from a frame, and lowered over a pulley into a ladle of molten iron. The instrument is suspended between the chain and lower rods, and contains a spiral spring similar to that used in a Salter's balance; this spring is arranged so that the ball and rods hang with their full weight upon the spring.

If the ball be kept well below the surface of the fluid metal it will, in expanding, and displacing the fluid, relieve the tension on the spring to an extent equivalent to the weight of the displaced metal.

The spring is placed in a brass frame, on which is also mounted a cylinder, which revolves uniformly by clockwork. A pencil attached to the moving end of the spring presses against a sheet of paper wound round the cylinder. This vertical

motion of the pencil, when combined with the horizontal motion of the paper on
the revolving cylinder, produces the curve of volume.

The first operation is to hang a rod on the spring balance with a piece of wrought
iron at the end, which is an exact facsimile of that part of the shank of wrought
iron fixed in each ball which will eventually protrude above the molten iron when
the ball is submerged. This weight brings down the spring balance to indicate from
1 to 2 lbs. The cylinder is then thrown out of gear and moved round, the pencil
making a straight zero line, which represents the position when the cold and molten
iron have the same specific gravity. The small piece of iron representing the upper
part of the shank is then removed, and the actual ball put in place. This ball has
been accurately weighed before, and its specific gravity also taken. Hanging it
on the spring balance brings the index below the zero or equilibrium line. The ball
is now lowered into the metal, the clockwork having been previously put in action.
A diagram is thus drawn during the heating and melting of the ball, of which the
vertical ordinates represent change of volume in ounces of increased displacement, and
the horizontal element represents time in minutes.

A number of diagrams were taken with 3-inch and 4-inch diameter balls, the specific
gravities of which had previously been ascertained. The general character of these
is shown on fig. 1, which is one of the numerous diagrams taken, in which B, F
represents the liquid volume, and A, B, C, D, E, F the changing volume in passing
from the solid to the liquid state.

Fig. 1.

4-inch ball of No. 4 foundry iron (Cleveland); poured from very hot
metal; immersed in No. 4 foundry iron.

Weight of ball and immersed part of stalk . . . . 132 oz.
Specific gravity of ball, and immersed part of stalk . 6·95
Maximum sinking effect . . . . . . . . . . . . . . . . 2 oz.
Maximum floating effect . . . . . . . . . . . . . . . . 11 "
Specific gravity of fluid iron = \( \frac{6.95 \times 130}{132} \) = 6·84
Specific gravity of plastic metal = \( \frac{6.95 \times 130}{143} \) = 6·32

Between A and B, fig. 1, the average density of the ball changes, until at B it has
become the same as that of the molten iron. It is at this point that a freely floating ball would just appear at the surface. The expansion beyond this corresponds to the gradual rising of a free ball above the surface, the disturbances in the flotation due to the cooling of the emergent part of the ball, and to the interference of the floating scoria in the more crude experiment, are obviated by keeping the ball submerged.

As the ball becomes hotter the curve flattens between C and D, the conduction of the heat into the ball becoming slower, until no further expansion takes place. Several balls, removed at this stage, were found complete in form, but so soft that a steel pin could be pushed right through them. This plastic condition of the mass remains for a short time, when it quickly passes into the liquid condition, the metal of the ball joining the molten iron in the ladle. Of course, so soon as the melting of the ball begins, the pencil no longer registers measurable changes of volume, as a reduction of mass is taking place, but the maximum volume of the ball can be measured in the plastic condition, and the volume when it reaches the liquid condition being known, it can be stated with certainty that it passes rapidly from one condition to the other. The conducting power of iron is so good that little wasting of the surface takes place, until the whole ball from surface to centre is in a plastic condition, and then it very rapidly melts and joins the bath; as shown by the sudden drop of the curve at E.

The mean average of a number of experiments upon grey Cleveland iron led me to conclude that the

Specific gravity of the solid iron at atmospheric temperature was 6.95
That the specific gravity of the molten iron was . . . . . 6.88
That the specific gravity of the plastic iron was . . . . . 6.50

In other words, while cast iron passes from the solid to the liquid state its volume is at its minimum when the mass is solid. As the temperature rises the metal first expands 1.02 per cent., and then has the same specific gravity as the liquid metal, viz., 6.88. It then continues expanding until it reaches the plastic condition, when it assumes its maximum volume with a specific gravity of 6.5, the total increase of volume from the solid to the plastic state amounting to 6.92 per cent.

After this, expansion by heat ceases and a quick contraction takes place, until the mass becomes liquid, when its specific gravity is, as before, 6.88. If this is expressed in terms of the volume of liquid iron, taken as 100, the volume of the solid iron at atmospheric temperature is 98.98. That of plastic iron is 105.85, in which condition an increase of heat to the melting point reduces the volume to 100, representing its liquid condition.

These changes of volume were much greater than was expected, and it was thought well to verify them by a converse series of experiments which enabled the changes in a cast iron ball in passing from the liquid to the solid state to be observed. Two
spherical moulds of dried loam were made 15.09 and 15.28 inches diameter respectively. Into these, molten iron was poured, in the former case, Cleveland white iron, and in the latter, Cleveland grey iron. A few minutes after the iron was run, the top of the mould was raised and the diameter of the congealed surface measured with callipers. This was continued at intervals of time, and the diagram, fig. 2, shows the gradual increase of diameter of the grey and white iron balls as they cooled.

The large size of the balls made the cooling a slow process, and the horizontal line representing time could not conveniently be extended in a diagram, but the final diameter, when the balls, after ten or twelve hours, became cold, is shown. The general result is a qualitative confirmation of the previous experiments, although not quantitative, as the early consolidation of the outer layers of metal prevents the free expansion of the interior.

These experiments were made in 1879–80, and proved that grey iron and white iron possessed the property of expanding when cooling, and contracting when heating, within a range of temperature approaching the melting points, and to an extent near that found in the case of water, which in solidifying expands in volume 9.3 per cent., while grey iron expands nearly 6 per cent., and white iron even more; the approximation appearing to indicate that the phenomena were of the same order.

These facts led me to suggest that the phenomena of regelation and welding
might probably prove to be identical. I afterwards found that the same suggestion
had been made by Love.* As, however, this hypothesis was not based on a know-
ledge of the properties of wrought iron, which can be welded, but upon those of cast
iron, which cannot be welded, it appeared that the suggestion could only be regarded
as speculative, until some method of examining the physical properties of wrought
iron within the range of temperature known as the welding heat could be devised.

This brief statement of my earlier researches† will serve to lead to the work
embodied in the present paper, which shows that wrought iron at the welding
temperature possesses the property of expanding when cooled and contracting when
heated, and that the welding property is intimately connected with the critical
condition in which this abnormal behaviour is exhibited.

Professor James Thomson was the first to show that although in the case of
normal bodies which expand by heat and contract by cold, the effect of impact or of
pressure is to heat them; theoretical considerations rendered it probable that in
a material which possessed the physical property of expanding during cooling and
contracting during heating, a contrary effect would be produced. The effect of
pressure or impact would cool and not heat it. This was subsequently experimentally
demonstrated, in the case of freezing water, by Lord Kelvin.‡

These theoretical deductions of Professor James Thomson, and the well-known
confirmatory experiments by Lord Kelvin, led to a theory of regelation now
generally accepted, which depends upon the lowering of the solidifying (or freezing)
point by pressure.

The condition known as "the welding state" of iron or steel is one which exists
only within a very limited range of temperature. If the smith takes his iron bars
out of the fire at too low a temperature welding cannot be effected. If, on the other
hand, the iron is too hot, a failure is also certain.

The range of temperature during which impact or pressure causes the union known
as the welding of two masses of iron or steel, is therefore comprised within narrow
limits, and the familiar operation is really a critical one.

In order that the phenomenon of the welding of iron may be identified with
the regelation of ice, it must be experimentally proved that the surfaces of the iron,
at the moment of welding, are in that peculiar and critical condition in which an
increase of heat will cause contraction and a diminution of heat will be followed by
the expansion of the mass. On the other hand the identification of regelation and
welding will be equally satisfactory if the collateral property of the cooling of the
hot iron by pressure or impact can be demonstrated.

The first method of demonstration is impracticable, as the welding state is transient

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* Proceedings of Civil and Mechanical Engineering Society, February 19th, 1880.
† Proc. Iron and Steel Institute, 1879-80.
and only affects a portion of the mass, so that methods which are available for measuring changes of volume in cast iron are inapplicable.

The only method of proof left open was to show that pressing the welding masses is attended by a fall in their temperature.

Unfortunately, fourteen years ago, when I made my earlier experiments, the investigation could not be continued as there was no suitable pyrometer with which such a delicate experiment could be carried out.

The recent successful application to metallurgical research, by Professor Roberts-Austen, of a recording pyrometer,* led me to resume the investigation of the question.

This pyrometer, which depends upon the use of a thermo-junction, consisting of a platinum wire twisted with another wire of platinum alloyed with 10 per cent. of rhodium, had been of service in the investigation of critical temperatures in various metals and alloys, and as Professor Roberts-Austen offered to place his laboratory and appliances at my disposal, and to aid me by advice, the opportunity for conducting the new experiments was gladly accepted.

The first experiments were made by placing the thermo-couple between the two welding faces of bars heated in an ordinary smith's fire. The wires of the thermo-couple were carried from the smith's shop to the pyrometer in the laboratory, but signalling was necessary to ensure the taking of the photographic record of the temperature at the exact moment the smith applied pressure, and it soon became evident that the arrangement was awkward. The results were far from being uniform, although on several occasions a distinct fall of temperature was apparent when welding was effected, which encouraged the expectation that with a more perfect system of work the true facts of the case would be revealed.

After full consideration it was decided that the only satisfactory way to proceed would be to use the electric welding apparatus of Thompson Houston with alternating currents. The Electric Welding Company readily put one of their admirable appliances and a suitable dynamo at my disposal; the manager, Mr. Armstrong, and the electrician, Mr. Reif, assisted in installing it at the Mint, and helped in every way to make the arrangement effective. By the kindness of Mr. R. A. Hill, Superintendent of the Operative Department, the composite alternating dynamo was driven from the Mint engines, and the conductors from the dynamo were carried over the intervening buildings to Professor Roberts-Austen's laboratory, where they were connected to the electric welder.

The wires of the thermo-junction, which was placed in contact with the surfaces to be welded, were carried from the welder, round the walls of the laboratory to the galvanometer placed inside the camera of the recording pyrometer.

It may be well to point out that the deflection of the galvanometer mirror causes a

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spot of light to move horizontally across the plate in the photographic slide, which slide moves vertically upwards at a uniform speed controlled by clockwork. The spot of light thus describes a curve, the ordinates of which represent respectively temperature and time. By this means a photographic record is produced. A base line (also produced by photography) represents the zero of temperature. When the indications of the thermo-junction are calibrated the diagram affords a complete record of the changes of temperature in the material in contact with the thermo-junction.

Plate 1, figs. 1 and 2, were the first taken, and some transient surprise was caused by finding that on the pressure being applied, by a hand lever acting on a pinion and rack, there was a rise instead of a fall of temperature. On reflection it appeared that this would certainly be due to the distortion and crushing up of the soft heated iron when the bars were pressed together at the welding temperature. Work was thus done, and the heat evolved masked any true fall of temperature.

To get rid of this heat of distortion it was necessary to confine the bar when pressed in some rigid envelope, which, from the conditions of the experiment, must, because of the electric current used for the heating, be a non-conductor of electricity.

After many attempts and failures the plan was adopted of placing the bar inside a close-fitting cylinder of porcelain, outside of which was closely fitted a strong steel die.

Both porcelain cylinder and steel die were cut through the centre in a plane transverse to the axis. This plan enabled the wires of the thermo-junction to be led to the centre of the bar, where the maximum heat was evolved. The bar was perforated by a minute hole, into which the wires forming the thermo-junction passed from each side.

Fig. 3.

Pipe-clay insulators encircled the wires and rested in grooves between the faces of the transverse cut, through the die, so as to prevent contact between the die and the wire.

After the temperature of welding had been noted on a series of photographic plates, there was no object in severing the bar so as to make a welded junction for each experiment.
All that was necessary was to heat by electricity in the electric welder a continuous bar until the position of the spot of light on the scale made it certain that the temperature was within the welding limits in the neighbourhood of the thermo-junction. The pressure was then applied.

When the bar was raised to welding heat inside the cylinder of porcelain, the pressure was applied. The time of its application is marked P on the photographic curve in each case. The position of this point was indicated by a signal made by momentarily obscuring the light which fell on the galvanometer mirror, thereby producing a brief interruption to the continuity of the curve.

These signals could be varied at will and proved to be of great service (see Plate 1, figs. 3, 4, 4a, 5, 6 and 7).

The current which heated the bar was not entirely cut off. This was done to avoid any fall of temperature before the pressure was put on, and in some of the diagrams it will be seen that it has not always been possible to avoid a slight and uniform rise, which merely means that the current of the electric welder did something more than counterbalance the loss of heat by radiation.

The pressure was applied when the temperature of the bar was 1347° C. (see Plate 1, fig. 3). A sudden rise of 27° C. showed itself, but a rise in temperature might be expected to take place, until all interstices between the outside of the bar and the envelope were filled by the plastic iron. The porcelain of course cracked, and the minute cracks had also to be filled before the effect of pressure in producing a fall in temperature could be demonstrated.

The second time the bar was heated to 1371° C., and on pressing a rise of temperature equal to 8° C. was shown (see Plate 1, fig. 4).

This small rise appeared to indicate that the interstices were nearly, or quite filled. The third time the same bar was heated to 1420° C. and pressed, a distinct fall of 27° C. was indicated by the diagram, thus for the first time realizing the anticipation with which I began the investigation (see Plate 1, fig. 5).

The fourth time the bar was heated to 1400° C., when a pressure of about 1200 pounds per square inch of the area of the bar, or 80 atmospheres, gave the remarkable fall of 57° C. (see Plate 1 fig. 6).

The fifth time the bar was heated to 1300° C., a much lower temperature than the last, when, on being pressed, the fall in temperature was recorded as 19° C. (see Plate 1, fig. 7).

If the bar experimented on be examined, a number of vein-like protuberances will be seen, showing that the plastic iron had to fill the crevices in the cracked porcelain, before the pressure could cause a fall of temperature.

It appears from the series of experiments on this bar, that the limits of temperature within which the thermal expansion is negative, certainly include a range between 1300° C. and 1420° C., and they may extend both above and below these limits, although, the fall being only 19° C. at the lower temperature as compared with 57° C. at the higher, it looks as if the lower temperature were approaching the limit,
STEEL AT WELDING TEMPERATURES.

No doubt a series of experiments to determine the exact limits of the critical state would be full of interest.

Between the temperature of 1400° and that of melting wrought iron (stated to be 1600°) there are doubtless increasing degrees of mobility in the material. When pressure is put on the bar, say at 1400°, it not only lowers the temperature of the melting point, but increases the mobility at lower temperatures, so that if before pressure the temperature be 1400°, after pressure there may be a condition of mobility between the molecules which corresponds to a temperature without pressure of 1500°, although the temperature has been reduced by pressure to 1343°.

If two pieces of iron, or almost any metal, be raised to the melting point, union can no doubt be effected, but this is by melting together and not by welding. The process of welding appears to be that by which complete union can be effected by hammering or pressure, at a temperature considerably below that required to melt the material. The heat of the fire having raised the bars within the critical range of temperature above described, the smith in striking with his hammer is assisted by the special properties of this welding material in producing an increased mobility of the molecules, which approach though never arrive at liquidity. This condition is favourable to the interpenetration of the molecules, and consequent adhesion of the surfaces on hammering.

Since I made this experiment in Professor Roberts-Austen’s laboratory, I have had the opportunity of experimenting in steel works upon the behaviour of solid masses of soft weldable rolled steel when lowered into molten steel of the same quality. The mass at first sinks, and then quickly floats to the surface, where it remains until melted, showing that weldable low carbon steel follows the same law as cast iron, and therefore possesses that property which it is contended is essential to bodies which can be united by the process of regelation or welding. The increase of carbon in steel appears to prevent welding just as it does in the case of the more highly carbonized form of iron known as cast iron.

In conclusion I would observe that if I have been able to demonstrate this remarkable property in wrought iron of being cooled by pressure when at the welding temperature, it would not have been possible to attain this result without the aid of Professor Roberts-Austen’s admirable pyrometer, and without the help which he and his able assistants, Mr. Stansfield and Mr. Reginald Roberts, have contributed.

Explanation of Plate.

Effect of Pressure on an Iron Bar.

Fig. 1.—Current cut off before pressure.
Fig. 2.—”, ” at a lower temperature.

In each experiment pressure applied at point marked P.
Effect of Pressure in a series of Five Experiments on an Iron Bar 1/2" in diameter, enclosed in a Porcelain and Steel Cylinder.

1st Experiment.—Fig. 3 at a temperature of 1347° C. gave a rise of 27° C.

2nd " —Fig. 4 " 1371° C. " 8° C.

Fig. 4A is a diagram produced at the same time as fig. 2, but from a more sensitive galvanometer. The same scale of temperature is not applicable.

In each experiment pressure applied at time marked P.

Fig. 5.—3rd Experiment at 1420° C. pressure gave a fall of 27° C.

Fig. 6.—4th " at 1400° C. " 57° C.

Fig. 7.—5th " at 1300° C. " 19° C.

In each experiment pressure applied at time marked P between first two signals, and relieved between last two signals. The current was cut off immediately after the fourth signal.