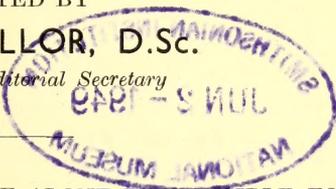


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FOR
1947
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Parts I-IV

EDITED BY
D. P. MELLOR, D.Sc.
Honorary Editorial Secretary



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P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

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1944		Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney.
1938	P 2	‡Albert, Adrien, Ph.D. <i>Lond.</i> , B.sc. <i>Syd.</i> , A.R.I.C. <i>Gt. B.</i> , Commonwealth Research Fellow in Organic Chemistry, University of Sydney; p.r. "Greenknowe," Greenknowe-avenue, Potts Point.
1935		‡Albert, Michel Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		‡Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		‡Alldis, Victor le Roy, I.S., Registered Surveyor, Box 57, Orange, N.S.W.
1909	P 12	‡Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Camb.</i> , A.M.I.E. <i>Aust.</i> , Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1945		Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 2	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1946	P 1	Barclay, Gordon Alfred, Chemistry Department, Sydney Technical College, Harris Street, Ultimo, N.S.W.; p.r. 78 Alt Street, Ashfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1946	P 4	Beattie, Joan Marian (Mrs.), B.Sc., Box 92, P.O., Cobar.
1947		Beckmann, Peter, A.S.T.C., Chemist, Staff Hostel, Glen Davis, N.S.W.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. (<i>Oxon.</i>), 6 Beechcroft-road, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 26A Wolseley-road, Mosman.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills.
1946		Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carabella-street, Kirribilli.
1933	P 28	Bolliger, Adolph, Ph.D., F.A.C.I., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.)
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., International Wool Secretariat, Dorland House, 18 Regent-street, London, S.W.1. (President, 1935.)
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1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney; p.r. 19 Handley-avenue, Thornleigh.

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- 1946 Breyer, Bruno, M.D., Ph.D., M.A., Lecturer in Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Sydney.
- 1940 Brigden, Alan Charles, B.Sc., 8 Clifford-avenue, Manly.
- 1919 P 1 Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
- 1942 Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
- 1935 P 4 Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
- 1945 Brown, Norma Dorothy (Mrs.), B.Sc., Biochemist, 58 Hopetoun-avenue, Vaucluse, N.S.W.
- 1941 Brown, Samuel Raymond, A.C.A. Aust., 87 Ashley-street, Chatswood.
- 1913 P 22 †Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
- 1947 Buchanan, Gregory Stewart, B.Sc. (Hons.), Lecturer in Physical Chemistry, Sydney Technical College; p.r. 51 Argyle-street, Ryde, N.S.W.
- 1940 Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
- 1946 Bullen, Keith Edward, M.A., B.Sc. N.Z., M.A. Melb., Ph.D., sc.D. Camb., Professor of Applied Mathematics, University of Sydney, Sydney, N.S.W.
- 1898 †Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. Syd., F.R.A.C.S., "Radstoake," Elizabeth Bay.
- 1926 Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
- 1940 P 1 Cane, Reginald Frank, D.Sc., A.A.C.I., General Motors-Holdens Ltd., Fishermen's Bend, Melbourne, Victoria; p.r. 2 David-street, St. Kilda, S.2.
- 1940 Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
- 1938 P 2 Carey, Samuel Warren, D.Sc., Professor of Geology, University of Tasmania, Tasmania.
- 1903 P 5 †Carslaw, Horatio Scott, sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
- 1945 Carter, Harold Burnell, B.V.Sc., Research Officer, C.S.I.R., McMaster Laboratory; p.r. Flat 4, 13 Milson-road, Cremorne.
- 1944 Cavill, George William Kenneth, M.Sc., c/o Department of Organic Chemistry, The University, Liverpool, Great Britain.
- 1913 P 4 †Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
- 1933 Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
- 1940 Chambers, Maxwell Clark, B.Sc., c/o Coty (England) Ltd., 35-41 Hutchinson-street, Moore Park; p.r. 58 Spencer-road, Killara.
- 1913 P 21 †Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
- 1935 P 2 Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
- 1935 Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
- 1938 Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
- 1941 Cohen, Max Charles, B.Sc., A.I.F., 80 "St. James," Stanley-street, Sydney.
- 1940 Cohen, Samuel Bernard, M.Sc., A.A.C.I., 34 Euroka-street, Northbridge.
- 1940 P 3 Colditz, Margaret Joyce, M.Sc., 9 Beach-street, Kogarah.
- 1940 P 2 Cole, Edward Ritchie, B.Sc., 7 Wolsten-avenue, Turrumurra.
- 1940 P 1 Cole, Joyce Marie, B.Sc., 7 Wolsten-avenue, Turrumurra.
- 1940 Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
- 1946 Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield.
- 1920 Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
- 1945 Coombes, Arthur Roylance, A.S.T.C. (Chem.), 14 Georges River-road, Croydon.
- 1913 P 5 †Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
- 1933 Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
- 1937 P 8 Cornforth, Rita Harriet, D.Phil. (Oxon.), M.Sc. (Syd.), c/o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
- 1940 Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
- 1919 Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
- 1909 P 7 †Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
- 1941 P 1 Craig, David Parker, Lecturer in Inorganic Chemistry, University of Sydney; p.r. 62 Springdale Rd., Killara.

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1921	P 1	†Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street., Rockdale.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1947		Curry, Gladys Olive (Mrs.), B.Sc. <i>Melb.</i> , F.R.I.C. <i>Gt. B.</i> , A.A.C.I., Director of Research, Australian Leather Research Association; p.r. "Cahors," No. 75, 117 Macleay-street, Pott's Point, N.S.W.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		†Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beauzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
1906		†Dixson, Sir William, "Merridong," Gordon-road, Killara.
1913	P 3	†Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1946		Donohoo, Norma Winifred, B.Sc., 41 Second-street, Ashbury.
1947		Downes, Alan Marchant, B.Sc. (Hons.), Railway-parade, Glenfield.
1943		Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
1937	P 10	Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney; p.r. 40 Manning-road, Double Bay. (President, 1947.)
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 39	Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney, Sydney.
1945		Eade, Ronald Arthur, B.Sc., 13 Steward-street, Leichhardt.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
1940		Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
1937		English, James Roland, L.S., Sydney.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1944		Erhart, John Charles, Chemical Engineer, c/o "Ciba" Coy., Basle, Switzerland.
1908		†Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. <i>Lond.</i> , A.R.A.I.A., 6 Major-street, Coogee.
1944		Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 338 Chapple-street, Broken Hill.
1939		Faull, Norman Augustus, B.Sc., A.Inst.P., c.o. National Standards Laboratory, University Grounds, City-road, Chippendale.
1909	P 7	†Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
1940		Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1933		Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street, Sydney.
1879		†Foreman, Joseph, M.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Edin.</i> , "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
1905		†Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1943		Frederick, Robert Desider Louis, B.E., 162 Buckley-street, Essendon, W.5, Victoria.
1940		Frenay, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
1944	P 2	Friend, James Alan, 16 Kelburn-road, Roseville.
1945		Furst, Hellmut Friedrich, B.D.S. (<i>Syd.</i>), D.M.D. (<i>Hamburg</i>), Dental Surgeon, 158 Bellevue-road, Bellevue Hill.
1935	P 2	Garretty, Michael Duhan, D.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.

Elected.	
1942	P 3 Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
1947	Gill, Naida Sugden (Miss), B.Sc., 45 Neville-street, Marrickville.
1947	†Gill, Stuart Frederic, School Teacher, 45 Neville-street, Marrickville.
1940	Gillis, Richard Galvin, 4 Tennyson-avenue, Caulfield, S.E.7, Victoria.
1945	Goddard, Roy Hamilton, F.C.A. Aust., Royal Exchange, Bridge-street, Sydney.
1947	Goldsworthy, Neil Ernest, M.B., Ch.M. Syd., Ph.D., D.T.M. & H. Camb., D.T.M. & H. Eng., D.P.H. Camb., 65 Roseville-avenue, Roseville.
1936	Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill.
1940	Graves, John Nevil, B.Sc., c/o Mr. R. Clarke, Ontava Ave., West Pennant Hills.
1938	Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
1946	Gutmann, Felix, Ph.D., Commonwealth Research Fellow, Faculty of Agriculture, University of Sydney, Sydney.
1947	Hall, Lennard Robert, B.Sc., Geological Survey, Department of Mines, Bridge-street, Sydney.
1945	Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney.
1934	Hall, Norman Frederick Blake, M.Sc., Chemist, 15A Wharf-road, Longueville.
1892	†Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill.
1940	P 9 Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney.
1905	P 6 †Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
1936	Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1934	Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1946	Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney.
1929	Hawley, J. William, J.P., Financial Agent.
1934	Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 34 Nicholson-street, Chatswood.
1919	Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1945	Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd.; p.r. 10 Cremorne-road, Cremorne.
1938	P 4 Hill, Dorothy, M.Sc. Q'ld., Ph.D. Cantab., Geological Research Fellow, University of Queensland, Brisbane.
1946	Hinder, Nora (Miss), B.Sc. Syd., 22 Chester-street, Epping.
1936	Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
1928	Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), "St. Cloud," Beaconsfield-road, Chatswood.
1916	Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, 81 Frederick-street, Rockdale.
1941	Howard, Harold Theodore Clyde, B.Sc., Principal, Technical College, Granville.
1935	Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1938	P 8 Hughes, Gordon Kingsley, B.Sc., Department of Chemistry, University of Sydney, Sydney.
1947	Humpoletz, Justin Ernst, B.Sc. Syd., 21 Belgium-avenue, Roseville.
1923	P 3 †Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
1943	Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville.
1942	P 1 Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
1940	Johns, Thomas Harley, M.Sc., 130 Smith-street, Summer Hill.
1946	Johnson, Guy Frederick, 644 Botany-road, Alexandria.
1909	P 15 Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)

Elected.	
1935	P 6 Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1930	Judd, William Percy, 123 Wollongong-road, Arncliffe.
1935	Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
1940	Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1 Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934	Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove.
1943	Kimble, Jean Annie, Research Chemist, B.Sc., 383 Marrickville-road, Marrickville.
1920	Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.
1939	P 1 Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936	Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., Scientific Liaison Officer, Victoria Barracks, Melbourne, Victoria.
1946	Lederer, Michael, 67 Edgecliff-road, Bondi Junction.
1947	Le Fevre, Raymond James Wood, D.Sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney.
1936	P 2 Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards.
1920	Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 56 †Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.)
1942	Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 3 Lipson, Menzie, B.Sc., A.A.C.I., Chemist, c/o Department of Textile Industry, Leeds University, Leeds 2, England.
1947	Lloyd, James Charles, B.Sc. <i>Syd.</i> , N.S.W. Geological Survey, 41 Goulburn-street, Liverpool.
1940	P 1 Lockwood, William Hutton, B.Sc., Food and Agricultural Division, Control Commission for Germany (B.E.), Berlin, B.A.O.R., Germany.
1906	†Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1943	†Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park.
1945	Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1942	Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 84 Marine-parade, Maroubra.
1939	P 4 Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1943	McCoy, William Kevin, Analytical Chemist, R.A.A.F.; p.r. 16 Bishop's-avenue, Randwick.
1940	McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940	McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2 †McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1 †McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P 7 McKenzie, Hugh Albert, B.Sc., Assistant Research Officer, C.S.I.R.; p.r. 52 Bolton-street, Guildford.
1943	McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Technological Museum, Harris-street, Ultimo; p.r. 14 Orwell-street, Potts Point.
1932	McKie, Rev. Ernest Norman, B.A. <i>Syd.</i> , St. Columba's Manse, Guyra.
1947	McMahon, Patrick Reginald, M.Agr.Sc. <i>N.Z.</i> , Ph.D. <i>Leeds</i> , A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney.
1927	McMaster, Sir Frederick Duncan, kt., "Dalkeith," Cassilis, N.S.W.
1943	McNamara, Barbara Joyce (Mrs.), M.B., B.S., Dimbulah, North Queensland.
1946	McPherson, John Charters, "Greenleys," No. 6 Wallaringa-avenue, Neutral Bay.
1946	P 1 McRoberts, Helen May, B.Sc., New England University College, Armidale.
1947	Magee, Charles Joseph, D.Sc.Agr.†. <i>Syd.</i> , M.Sc. <i>Wis.</i> , Chief Biologist, Department of Agriculture; p.r. 4 Alexander-parade, Roseville.

Elected.

- 1945 Makepeace, Barbara (Mrs.), B.Sc., Biochemist, 5 Jenkin-street, Chatswood.
- 1947 Maley, Leo Edmund, B.Sc. (Hons.), 116 Maitland-road, Mayfield.
- 1940 Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
- 1947 Mapstone, George E., M.Sc., A.A.C.I., M.Inst.Pet., Chief Chemist of National Oil Pty. Ltd., Glen Davis; p.r. 2 Anderson Square, Glen Davis, N.S.W.
- 1944 Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
- 1946 May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill.
- 1935 P 1 Maze, Wilson Harold, M.Sc., Deputy Registrar, University of Sydney, Sydney.
- 1912 † Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
- 1929 P 24 Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.)
- 1941 Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
- 1940 Mercer, Edgar Howard, Textile Department, University of Leeds, Leeds, England.
- 1928 Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, "Walla Walla," Hull-road, Beecroft.
- 1940 Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd. 15 Shaw-avenue, Earlwood.
- 1943 Molloy, Ernest Patrick, Assistant Sectional Manager, 129 Gibbes-street, Rockdale.
- 1945 Morris, Samuel, A.S.T.C. (Chem.), A.A.C.I., F.C.S.G.B., 217 Burns Bay-road, Lane Cove.
- 1941 Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
- 1922 P 27 Morrison, Frank Richard, A.A.C.I., F.C.S., Economic Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo.
- 1934 Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
- 1944 Moye, Daniel George, Chemist, Warragamba Dam.
- 1946 Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney.
- 1915 Murphy, Robert Kenneth, Dr. Ing., Chem. Eng., A.S.T.C., M.I.Chem.E., F.A.C.I., Principal, Sydney Technical College, Sydney.
- 1923 P 2 Murray, Jack Keith, B.A., B.Sc. Agr., Government House, Port Moresby, Papua.
- 1930 P 6 Naylor, George Francis King, M.A., M.Sc., Dip. Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld.
- 1943 Neuhaus, John William George, 190 Old Prospect-road, Wentworthville.
- 1932 Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Botany, Victoria University College, P.O. Box 1580, Wellington, N.Z.
- 1943 Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. No. 2 Flat, corner Hendy-avenue and Rainbow-streets, Coogee.
- 1935 Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
- 1945 P 1 Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T.
- 1938 P 1 Noble, Norman Scott, D.Sc. Agr., M.Sc., D.I.C., c/o C.S.I.R., 314 Albert-street, East Melbourne, Vic.
- 1920 P 4 † Noble, Robert Jackson, M.Sc., B.Sc. Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
- 1947 Nordon, Peter, A.S.T.C., A.A.C.I., Chemical Engineer, 1 Edgecliff-road, Bondi Junction.
- 1940 P 25 Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
- 1935 P 4 O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
- 1947 Old, Adrian Noel, B.Sc. Agr., Chemist, Department of Agriculture; p.r. 4 Springfield-avenue, Pott's Point.
- 1921 P 6 Osborne, George Davenport, D.Sc. *Sydl.*, Ph.D. *Camb.*, Lecturer and Demonstrator in Geology in the University of Sydney. (President, 1944.)
- 1920 P 74 Penfold, Arthur Ramon, F.A.C.I., F.C.S., Director, Museum of Technology and Applied Science, Harris-street, Ultimo. (President, 1931.)
- 1938 Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
- 1935 Phillips, Orwell, 55 Darling Point-road, Edgecliff.

Elected.

- 1946 Pinwell, Norman, B.A. (*Q'land*), The Scots College, Bellevue Hill.
- 1943 Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
- 1919 Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
- 1896 †Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
- 1946 Potter, Bryce Harrison, B.Sc. (Hons.) (*Syd.*), 13 Fuller's-road, Chatswood.
- 1921 P 2 Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
- 1938 Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
- 1945 Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst.
- 1927 Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
- 1918 P 1 Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
- 1945 Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood.
- 1893 †Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
- 1935 P 3 †Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
- 1922 P 6 Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
- 1940 P 2 Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
- 1919 P 3 Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
- 1936 Randall, Harry, Buena Vista-avenue, Denistone.
- 1947 Ray, Nancy Evelyn (Mrs.), Plastics Manufacturer, 14 Hedger-avenue, Ashfield.
- 1947 Ray, Reginald John, Plastics Manufacturer and Research Chemist, 14 Hedger-avenue, Ashfield.
- 1931 P 1 Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, Vic.
- 1935 Reid, Cicero Augustus, 19 Newton-road, Strathfield.
- 1947 Reuter, Fritz Henry, Ph.D. (*Berlin*, 1930), F.A.C.I., 94 Onslow-street, Rose Bay.
- 1946 Rhodes-Smith, Cecil, 261 George-street, Sydney.
- 1947 Ritchie, Arthur Sinclair, A.S.T.C., Lecturer in Mineralogy and Geology, Newcastle Technical College; p.r. 188 St. James-road, New Lambton, N.S.W.
- 1947 Ritchie, Bruce, B.Sc. (Hons.), c/o Pyco Products Pty. Ltd., 576 Parramatta-road, Petersham.
- 1939 P 15 Ritchie, Ernest, M.Sc., Senior Lecturer, Chemistry Department, University of Sydney, Sydney.
- 1939 P 3 Robbins, Elizabeth Marie (Mrs.), M.Sc., 36 Cambridge-street, Epping.
- 1933 Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
- 1940 Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush; p.r. Flat 4, 43 Johnston-street, Annandale.
- 1935 P 2 Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
- 1940 Rosenbaum, Sidney, 44 Gildershorp-avenue, Randwick.
- 1940 Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
- 1945 Rountree, Phyllis Margaret, M.Sc. *Melb.*, Dip.Bact. *Lond.*, 25 Elizabeth Bay-road, Elizabeth Bay.
- 1945 Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory; p.r. 83 Woniora-road, Hurstville.
- 1945 Sampson, Aileen (Mrs.), Sc.Dip. (A.S.T.C., 1944), 9 Knox-avenue, Epping.
- 1935 Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
- 1941 P 3 Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, 60 Boundary-street, Roseville.

Elected.

- 1920 Scammell, Rupert Boswood, B.Sc. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
- 1946 P 1 Scott, Beryl (Miss), B.Sc., 314 Rowe-street, Eastwood.
- 1940 Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
- 1933 Selby, Esmond Jacob, Dip.com., Sales Manager, Box 175 D, G.P.O., Sydney.
- 1936 Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
- 1938 Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, c/o Shell Co. of Aust., 163 William-street, Melbourne, C.I, Vic.
- 1936 P 2 Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. *Melb.*, 43 Robertson-road, Centennial Park.
- 1945 Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
- 1917 Sibley, Samuel Edward, Mount-street, Coogee.
- 1945 P 2 Simmons, Lewis Michael, B.Sc. (Hons.) *Lond.*, Ph.D. *Lond.*, F.A.C.I., Head of Science Department, Scots College; p.r. The Scots College, Victoria-road, Bellevue Hill.
- 1943 Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
- 1933 Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiatea," Oyama-avenue, Manly.
- 1940 Smith, Eric Brian Jeffcoat, New College, Oxford, England.
- 1947 Smith-White, William Broderick, M.A. *Cantab.*, B.Sc. *Syd.*, Department of Mathematics, University of Sydney; p.r. 7 Henson-street, Summer Hill.
- 1919 Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
- 1921 Spencer-Watts, Arthur, "Araboono," Glebe-street, Randwick.
- 1916 Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
- 1914 Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
- 1900 P 1 †Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
- 1942 Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
- 1916 P 1 Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney; p.r. 79 Ocean-street, Woollahra.
- 1940 Stroud, Richard Harris, B.Sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.
- 1918 †Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
- 1919 †Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.
- 1920 Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
- 1941 P 2 Swanson, Thomas Baikie, M.Sc. *Adel.*, c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.
- 1915 P 3 Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
- 1944 Thomas, Andrew David, Squadron Leader, R.A.A.F., M.Sc., A.Inst.P. 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic.
- 1946 Thomas, Ifor Morris, M.Sc., Department of Zoology, University of Adelaide, Adelaide, S.A.
- 1919 Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
- 1935 Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
- 1923 Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
- 1940 Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
- 1943 Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.

Elected.

- 1940 Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co.,
1 O'Connell-street, Sydney.
- 1921 Vicars, Robert, Marrickville Woollen Mills, Marrickville.
- 1935 Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The
Promenade, Cheltenham.
- 1933 P 5 Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New
England University College, Armidale.
- 1903 P 10 †Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the
University of Sydney; p.r. "Eightbells," Old Castle Hill-road, Castle Hill.
(President, 1930.)
- 1943 Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping.
- 1919 P 2 Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r.
45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
- 1945 Walters, Laurence Gordon, B.Sc., Flat 3, 33 Gould-street, Bondi.
- 1913 P 5 †Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator
in Biochemistry in the University of Sydney. (President, 1939.)
- 1944 Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T.
- 1921 †Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett,
Illoura-avenue, Wahroonga.
- 1919 P 1 Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology
in the University of Sydney.
- 1919 P 7 Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor of
Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue,
Lindfield. (President, 1937.)
- 1944 Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street,
North Sydney.
- 1941 P 1 Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of
Agriculture, University of Sydney.
- 1911 P 1 †Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of
Sydney; p.r. 64 Wentworth-road, Vacluse. (President, 1925.)
- 1936 Wearne, Harold Wallis, 6 Collingwood-street, Drummoyne.
- 1947 Webb, Gordon Keyes, A.F.I.A., A.C.I.S., Accountant, c/o Max Wurcker (1930)
Pty. Ltd., 99 York-street, Sydney.
- 1945 Webster, Evelyn May, B.Sc., Chemist, 2 Buena Vista-avenue, Mosman.
- 1920 Wellish, Edward Montague, M.A., Emeritus Professor of Applied Mathematics
in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
- 1921 Wenzholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agri-
culture, Sydney.
- 1947 Werner, Ronald Louis, Industrial Chemist, 25 Dine-street, Randwick.
- 1946 Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill.
- 1909 P 3 †White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, Uni-
versity Grounds, Newtown.
- 1943 Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street,
Sydney.
- 1928 Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram
Hall, Jersey-road, Strathfield.
- 1942 Williams, Gordon Roy, B.Sc., c.o. Davis Gelatine (Aust.) Pty. Ltd., Spring-
street, Botany.
- 1944 P 1 Willis, John Bryan, B.Sc., Demonstrator in Chemistry, University of
Sydney; p.r. Flat 2, Russell Hall, 17 Mount Street, Coogee.
- 1945 Willis, Jack Lehane, B.Sc., Flat 5, "Narooma", Hampden-street, North
Sydney.
- 1943 Winch, Leonard, B.Sc., 60 Baldwin-avenue, Asquith.
- 1940 Wogan, Samuel James, Range-road, Sarina, North Queensland.
- 1936 P 5 Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Government Astronomer,
Sydney Observatory, Sydney.
- 1906 P 12 †Woolnough, Walter George, D.Sc., F.G.S., c/o Mr. W. L. Woolnough, "Calla-
bonna", 8 Park-avenue, Gordon.
- 1916 Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 7
Wynyard-street, Sydney.
- 1946 Wyndham, Norman Richard, M.D., M.S. (*Syd.*), F.R.C.S. (*Eng.*), F.R.A.C.S.,
Surgeon, 225 Macquarie-street, Sydney.
- 1921 Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-
street, Sydney; p.r. Boomerang-street, Turramurra.

HONORARY MEMBERS.

Limited to Twenty.

Elected.

- | | |
|------|--|
| 1914 | Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England. |
| 1946 | Jones, Sir Harold Spencer, M.A., D.Sc., F.R.S., Astronomer Royal, Royal Observatory, Greenwich, London, S.E.10. |
| 1915 | Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A. |
| 1912 | Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England. |
| 1946 | Wood-Jones, F., D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (<i>Lond.</i>), F.R.S., F.Z.S., Professor of Anatomy, University of Manchester, England. |
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THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
- "The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
- "Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
- "The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front." By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E. D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.
1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.
1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.
1947. "The Teachers of Geology in Australian Universities." By Professor H. S. Summers, D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

- 1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 *George Bentham, C.M.G., F.R.S.
- 1880 *Professor Thos. Huxley, F.R.S.
- 1881 *Professor F. M'Coy, F.R.S., F.G.S.
- 1882 *Professor James Dwight Dana, LL.D.
- 1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

Awarded.

- 1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
 1886 *Professor L. G. De Koninck, M.D.
 1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
 1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
 1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
 1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
 1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
 1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
 1893 *Professor Ralph Tate, F.L.S., F.G.S.
 1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
 1895 *Robert Etheridge, Jnr.
 1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
 1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
 1901 *Edward John Eyre.
 1902 *F. Manson Bailey, C.M.G., F.L.S.
 1903 *Alfred William Howitt, D.Sc., F.G.S.
 1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
 1909 *Dr. Walter E. Roth, B.A.
 1912 *W. H. Twelvetrees, F.G.S.
 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
 1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
 1917 *Professor Sir Edgeworth David, K.B.E.; C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
 1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
 1920 *Joseph Edmund Carne, F.G.S.
 1921 *Joseph James Fletcher, M.A., B.Sc.
 1922 *Richard Thomas Baker, The Crescent, Cheltenham.
 1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
 1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
 1925 *Charles Hedley, F.L.S.
 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
 1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
 1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
 1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
 1935 *George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
 1938 *Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
 1939 *C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
 1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.
 1945 Professor William Noel Benson, B.A., D.Sc., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.
 1946 Black, J. M. A.L.S. (*honoris causa*), Adelaide, S.A.
 1947 *Hubert Lyman Clark, A.B. D.Sc., Ph.D., Hancock Foundation, U.S.C., Los Angeles, California.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
 1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
 1938 Frank Macfarlane Burnet, M.D. (Melb.), Ph.D. (Lond.), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
 1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.
 1947 John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
- 1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
- 1940 G. J. Burrows, B.Sc., University of Sydney.
- 1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.
- 1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.
- 1946 Briggs, L. H., D.Phil. (*Oxon.*), D.Sc. (*N.Z.*), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.
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ISSUED NOVEMBER 12, 1947

VOL. LXXXI

PART I

JOURNAL AND PROCEEDINGS
OF THE
ROYAL SOCIETY
OF NEW SOUTH WALES

FOR

1947

(INCORPORATED 1881)

PART I (pp. 1 to 76)

OF

VOL. LXXXI

Containing Papers read in April and May, with Plates I-II

EDITED BY

D. P. MELLOR, D.Sc.

Honorary Editorial Secretary

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE
STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN



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1947

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PRESIDENTIAL ADDRESS

By F. LIONS, B.Sc., Ph.D.

Delivered before the Royal Society of New South Wales, April 2, 1947.

PART I. GENERAL.

Ladies and Gentlemen :

The stated aim of the Royal Society of New South Wales is "to encourage studies and investigations in, and to receive at its stated meetings, and to publish, original papers on Science, Art, Literature and Philosophy, and especially on such subjects as tend to develop the resources of Australia, and to illustrate its natural history and productions".

As evidence of the efforts of the Society to live up to its aim, I have to report that 22 papers were accepted for reading and publication during the year, a pleasing feature being the variety of the subjects considered. This total does not nearly approach the record number of 50 papers read in the 1937-38 period, neither does it show any increase on the number presented last year. It might have been expected that the cessation of war would have led to a much greater volume of published work, but it must be remembered that the war effort required of the universities and technical colleges will not be completed for some years yet. When the strain of the excessive teaching duties imposed on the staffs of educational institutions has eased, it is confidently expected that their research output will again increase.

It takes very little consideration, too, to realise that a spate of papers embodying the results of completed researches will eventuate, because although the teaching strain at the moment is well-nigh intolerable, a record number of students is being initiated into the methods of science, and undoubtedly many of them will soon be able and eager to carry out original research work. Much of it should be published in the Society's Journal, but I cannot too strongly emphasise to the Society that now is the time to interest these embryo scientists in the work of this oldest scientific society in the State.

There is still a time lag in the publication of the Journal. Efforts are being made to get it printed and issued on the due dates, but the very great difficulties which beset the printing trade in this State at present militate against such a desirable result. The Council is properly concerned about the delays and is constantly endeavouring to accelerate publication. It should be pointed out to authors that they can assist very materially by correcting proofs promptly and returning them without delay to the editorial secretary.

During 1946 Lieutenant-General John Northcott, C.B., M.V.O., Commander-in-Chief of the British Commonwealth Forces of Occupation in Japan, was commissioned by His Majesty the King as Governor of New South Wales. He has been graciously pleased to accept the office of Patron of our Society, and the Society was honoured by his presence, together with that of his daughter, Miss Northcott, at the Society's Annual Dinner, which was held in the Sydney University Union Withdrawing Room on March 27th, 1947, and was well attended. The Society was also honoured by the presence of the Minister for Education, Mr. R. J. Heffron, and his wife, and there were many other

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guests. The function was of a high standard and was greatly enjoyed by all those who attended.

At the present time there are 314 ordinary members of the Society, and, with the two honorary members you have just elected, five honorary members. During the year we lost seven members by resignation and three by death. Twenty-two new members were elected during the year.

The attendance at our monthly meetings has been satisfactory, averaging 37, but with the passing of war-time and immediate post-war restrictions it is hoped that there will be even greater attendances at the ordinary monthly meetings. At these meetings the device of supplementing the reading of papers with exhibits, the screening of a film ("Eruption of Ruapehu") and lecturettes was again followed. In all, five lecturettes were given: by Mr. Chalmers ("Australian Gem Stones"), Dr. Mellor ("Synthetic Diamonds" and "New Instruments of Scientific Interest"), Dr. Still ("Some Recent Advances in Cellular Metabolism"), and Mr. Le Souef ("Consciousness and Instinct"). Mr. Faull exhibited a Geiger counter at the December meeting.

The Council has made strong representations to the Science House management committee for the installation of modern projection equipment in the main hall of Science House. Such equipment is now readily available from America, and, as those who attended last year's symposium on visual education methods must appreciate, its use could add considerably to the instruction and enjoyment of members and would undoubtedly increase the attendances at our monthly meetings.

Two symposia were held during the year, and proved to be very popular. The first was on "Energy Resources of the Commonwealth", the speakers being Dr. Dulhunty ("Fuel Energy"), Dr. Iredale ("Solar Energy") and Dr. Makinson ("Atomic Energy"). The second symposium dealt with "Tracer Elements", the speakers being Mr. Faull ("The Production and Measurement of Radio active Isotopes") and Dr. Rogers ("The Use of Radioactive Tracers in Biological Investigations").

The November meeting of the Society was devoted to a commemoration of great scientists, the speakers being Professor Elkin ("Boucher de Perthes—The Antiquity of Human Culture"), Mr. Smith-White ("Gottfried Wilhelm Leibnitz"), Mr. Wood ("Tycho Brahe") and Dr. Albert ("Valerius Cordus and the Pharmacopœia").

During the year five popular science lectures were given, the speakers being Mr. Fletcher ("Extinct Monsters"), Professor O'Neill ("A New Road for the Disabled Soldier"), Mr. Penfold ("Recent Developments in Plastics"), Miss Rountree ("The Smallest Forms of Life-Virus") and Dr. Hotten ("Triumph over Pain—The Story of Anæsthesia").

This year the Clarke Memorial Lecture was delivered by Professor L. A. Cotton, who chose as his subject "The Pulse of the Pacific". Despite the fact that on the night of the lecture the weather was appalling and that transport services were heavily restricted, he had a large and appreciative audience who, in turn, were amply rewarded by a most excellent lecture.

The Clarke Memorial Medal was awarded to Mr. J. M. Black, A.L.S. (*honoris causa*), of Adelaide, in recognition of his distinguished contributions to natural science in Australia. At the request of the Society the Medal was presented to Mr. Black by the President of the Royal Society of South Australia in Adelaide on Thursday, April 11th, 1946.

During 1946 Dr. L. H. Briggs, of Auckland University College, was invited to deliver the Liversidge Research Lectures. He chose as his subject "Plant Products of New Zealand", and delivered two very stimulating lectures. The importance of intensive plant product research in Australia was brought home during the war when it was shown that in certain species of *Duboisia* Australia

possessed some of the world's best sources of the alkaloids hyoscyne and hyoscyamine. Much the same position obtains now with respect to the glucoside rutin, which has been found to be of value in the treatment of capillary fragility associated with hypertension. Easily the best source of it so far reported is *Eucalyptus macrorhyncha*, the leaves of which contain 7-8%.

It is gratifying to note that the Council for Scientific and Industrial Research has appointed special officers to study the alkaloids in Australian plants, and that with their cooperation and, no doubt, stimulated by Dr. Briggs's lectures, some of the organic chemists at the University of Sydney have established a vigorous school of alkaloid research there. The stated aim of our Society emphasises our interest in the study of natural products, and may I say that soon again we hope to see renewed at the Technological Museum the work on essential oils that has been so badly interrupted by the war. There are some chemists in Australia who are of the opinion that work on natural products is out of date and unimportant when compared with what they are pleased to call "tailor-made molecules". It is quite a sobering experience to compare the efficiency of most tailor-made bacteriostatic drugs with that of the natural product penicillin; and it will be a sad day for science when Nature can present no more intriguing puzzles for scientists to unravel, or useful lessons for them to learn, for the elucidation of the complexities of natural phenomena has not just contributed to the enrichment of our sciences but has been their very flesh and blood and bone.

When we recall again the aim of our Society to develop the natural resources of Australia, we are particularly glad to congratulate the Minister of Education, Mr. Heffron, for his vision in establishing an Institute of Science and Technology in Sydney offering degree courses of study in science and engineering; and his wisdom in decreeing that the results of all research carried out in the Institute will be freely available to all. The scientific work of the United States of America has been greatly enriched in the past by the researches carried out in such famous institutes of technology as M.I.T. and Caltech.

During 1946 the Australian and New Zealand Association for the Advancement of Science resumed its nation-wide scientific conferences with a highly successful meeting at Adelaide. We rejoice at this evidence of the return of pre-war conditions, and extend our good wishes for the success of the A.A.N.Z.A.A.S. meeting at Perth this year.

It is gratifying to record that the finances of the Society remain in a healthy state. Once again the Government of New South Wales made a grant of £400, and this has been all the more welcome because of rising costs in the printing industry.

The number of books and parts of periodicals received by the library this year has noticeably increased, partly because of the receipt of back numbers delayed over the war period, partly because of extended changes. As a result of continued new accessions space in the library is becoming limited, and it will not be many years before a serious problem may arise. During the year a conference was arranged between representatives of the different owner bodies to consider the possibility of combining all three libraries in Science House into one when the extensions are undertaken in the future. However, unanimity on the proposal for unity put forward by the Royal Society was not attained. Mr. H. W. Wood has continued to act as Honorary Librarian during this year, and the thanks of the Society are due to him for his devotion to the best interests of the library.

Dr. Edgar Booth, a past President of this Society, of the Wool Secretariat, and Mr. Alan Maccoll, worthily represented the Society at commemoration celebrations in honour of Sir Isaac Newton held in London last July.

I should be ungrateful if I were not to express my appreciation for all the assistance and kindnesses I have received from the officers and Council of the Society during my year of office. At all times there has been willing assistance. Particularly, I should like to thank the Honorary Secretaries, Dr. D. P. Mellor and Mr. F. R. Morrison, and very especially Dr. Adolph Bolliger, on whom I leaned heavily for advice, and who took over the duties of the presidential office whilst I was abroad.

It is with regret that I announce the loss the Society has sustained through death, during the year, of three members.

HENRY GORDON FARNSWORTH (1877-1946) was a member of our Society since 1921. He joined the Public Works Department of this State when a young man, and rose to be Chief Inspector of the Stores Branch. He was particularly interested in lubricating oils and had built up a private laboratory for their testing. He was a noted horticulturist, being very fond of roses, and often planned gardens for his friends.

SIR GEORGE JULIUS, who died in June, 1946, joined the Royal Society of New South Wales in 1911. He was a graduate in Science and Engineering and won a high place in the scientific life of Australia. He played an important part in the founding and progressive development of the Institution of Engineers of Australia and the Standards Association. He will be chiefly remembered, however, for his work in connection with the Council for Scientific and Industrial Research, from the presidency of which he retired at the end of 1945. The achievements of the officers of the C.S.I.R. over the last twenty years are a tribute to his initiative, organising ability and forceful leadership. He played a big part in the Australian National Research Council and was a leader in the Rotary Movement. Probably he will be best remembered as the inventor of the totalisator, that practical calculating machine which was in some ways a forerunner of the amazing electronic calculating machines of today. He was also noted for his hobby—the building and operation of model railroads.

CARL ADOLF SUSSMILCH, was distinguished by his long and loyal service to the Royal Society. As a young man he became interested in geology and mining. Later he entered the service of the New South Wales Department of Education and was successively Lecturer-in-charge of the classes in Mining and Geology at Sydney Technical College, Principal of Newcastle Technical College, Assistant Superintendent of Technical Education, and before retiring, Acting Superintendent.

He was President of this Society in 1922, and served on the Council and in executive positions for many years. He was also President of the Linnean Society and Section C of the A.A.N.Z.A.A.S. Mr. Sussmilch was a great humanitarian, and did yeoman service for the Society of Crippled Children.

As a scientist he was chiefly known for his contributions to geomorphology and palæozoic stratigraphy. His book, "The Geology of New South Wales" was long a standard introduction to New South Wales stratigraphy and physiography.

PART II. FREEDOM OF SCIENCE.

Professor Elkin, in his Presidential Address to this Society in 1941, discussed the difficulty which confronts the retiring President, who, by tradition, is charged with the duty of preparing and delivering a Presidential Address to a quorum of the members. Traditionally, also, the first part of the address is a brief survey of the life of the Society and its interrelationships with the community during the preceding year. The choice of the subject matter of the second part of the address, however, has always been left to the personal decision of the retiring President. Usually, but not always, the form of this latter half has been that

of a review of the results of the President's own personal researches, combined with a survey of the special field containing those researches. Let me say here and now that I should have fallen into line with this conception of the requirements of the second half of the Presidential Address had it not been for an entirely unexpected happening during the year.

The American Philosophical Society, "held at Philadelphia for promoting useful knowledge", and the National Academy of Sciences of America, at Washington, D.C., decided last year to invite delegates from sister academies of science throughout the world to attend their autumn meetings in October of 1946, generously offering to defray all the expenses connected with the visits. I received a letter from Dr. Gates, President of the American Philosophical Society, and Dr. Jewett, President of the National Academy of Sciences, inviting me to nominate a representative of the Royal Society of New South Wales to attend the conferences. When the matter was put before the Council it was agreed that I, as President, should be the one to go to America.

In due course I travelled by air to Philadelphia and was there in time for the opening sessions of the American Philosophical Society's meeting. The meetings of the National Academy of Sciences followed, and at their conclusion I became one of a party of the visiting delegates who made a nation-wide inspection of important research centres in the United States of America.

The foreign delegates to Philadelphia and Washington came from many countries—from Australia, Belgium, Brazil, Canada, China, Czechoslovakia, Denmark, England, Finland, France, Greece, Holland, India, Italy, New Zealand, Norway, Peru, Roumania, Russia, Sweden and Switzerland. They had magnificent opportunities for getting to know one another, and the distinguished American scientists who acted as their hosts. Very many new personal friendships were formed as the result of the visits, and it is fair to say that the friendly meetings and personal exchange of ideas between scientists was at least as valuable a factor towards the reconstruction of some portion of the international community of science as were the important discussions which dealt with the formal machinery of international scientific cooperation, such as the International Scientific Unions and U.N.E.S.C.O.

Nevertheless, even to an Australian, from a land remote from the great centres of life and civilisation, where the inhabitants are inclined to regard the course of events in other lands with aloofness or frank disinterestedness, it was obvious that despite the intense longing and the utmost willingness of scientists from all parts of the world to return to the days when it could fairly be claimed that science belonged to all the world and had no national frontiers, and when scientists from all countries could meet simply as scientists and freely interchange ideas and friendly criticisms in a common search for truth, there was a conviction that such a return was not yet in prospect.

There was a general recognition that freedom of science, as we have known it, is in serious danger of being permanently disfavoured by the vast majority of the non-scientific community, and that the regimentation of scientists and the unrestricted use of the discoveries of science in time of war, seen now clearly for what they are—perversion of science—have brought mankind to the very brink of an abyss.

The dropping of atomic bombs on Hiroshima and Nagasaki, and the subsequent Bikini atoll tests have convinced all thinking persons that another great war would mean the end of civilisation as we know it. Let there be no doubt of that. Last week you heard what His Excellency Lieutenant-General Northcott had to say of Hiroshima and Nagasaki after personally inspecting what little remains of those once flourishing cities. That there is no defence against atomic bombs is attested by the most distinguished physical scientists who have had anything to do with their development. In America there is a

special committee headed by men like Einstein, Urey and Morse, charged with the duty of convincing all Americans that war in this atomic age is equivalent to national suicide.

Is there any wonder that, faced with such a prospect, unable to understand how it has been brought about, except that somehow or other scientists and science are heavily involved, the common man cries, "Enough of science!" That is the position the scientist of today faces. If he is to be allowed freely to carry on with his experiments and studies and freely to communicate his results to all the peoples of the world as before, then the non-scientific world has the right to demand that it be convinced that such freedom will not hasten a final disaster.

Before the falling of the first atom bombs there were many who were only too conscious of how destructively perversion of science was effecting human relationships. Hiroshima and Nagasaki brought it into sharp focus for all. Is it any wonder, then, that at Philadelphia and Washington there were still many doubts and forebodings and a feeling of frustration? Sir Henry Dale, who delivered the Pilgrim Trust lecture at Philadelphia, crystallised into words the vague perceptions of the many by discussing this very question of the Freedom of Science, and I should fail in my duty as your delegate to America were I not to bring to your notice some of the views he there expressed, or to do all I could to help to re-establish that international cooperation we once knew as the international community of science.

The physical scientist who looks back over the vast panorama of human history may be forgiven if he views it from a standpoint other than the traditional and sees the gradual progress of man in the control of his material environment as a step-by-step mastery over the sources of energy in Nature and their subjugation to the needs of life, rather than as a successive mastery over the materials employed for the making of weapons, such as the ages of stone, bronze, and iron. He can take some comfort from the realisation that mastery of the energy of fire has been applied, in the long run, to creative and beneficent ends, and that there has been a gradual evolution of civilisation from savagery. The progress has certainly not always been forward. There have been many setbacks, and the energy of fire has been frequently used to destroy much of man's achievements through the ages. This was vividly brought home to us by the great bombing raids of the war just ended. Man, in his mastery of the energy of fire, has always had the choice—whether to use it for the purposes of life, or for destruction.

Until the dropping of the first atomic bomb on Japan, the most significant event in the history of human progress occurred in the year 1774, when James Watt perfected the steam engine and showed how the energy of fire could be used to free man from the drudgery of animal labour. The scale on which man could live could then be pushed up according to the scale on which he could draw on the energy of fire to perform his mechanical tasks. Even with the steam engine, however, it would not have been a very much bigger scale had man remained dependent on the timber of the forests for fuel. It was the simultaneous tapping of the vast capital stores of fossil fuel, coal, locked up in the earth's crust back in the Permian and Carboniferous era, which enabled him to develop the invention of the steam engine so as to get ever-increasing amounts of mechanical energy for the purposes of life. For the first time in his history man possessed the power to push up his scale of living to any desired extent; and the scale on which a modern material civilisation can develop is dependent on the extent to which supplies of fossil fuel energy are available to it.

The great wars we have witnessed in these last thirty years have been, in the main, struggles for control of the sources of energy—as evidenced, for example, by the great German drive towards the Caucasian oilfields that was

stopped at Stalingrad. It is significant, too, that even at the present time much of the world unrest, as in Palestine and the East Indies, is in countries strategically located near great oilfields.

The earlier discoveries of physicists in their studies of radioactivity made it possible for them to visualise the possibility of artificial transmutation of elements, with the release of quantities of energy—atomic energy—of the order of a million times greater than what is obtainable from ordinary chemical reactions, such as the combustion of coal. Many of these earlier scientists also clearly foresaw, after the misuse of science in the 1914–18 war, that discovery of the means of unlocking supplies of atomic energy would be at once followed by attempts to prepare a super-bomb for the purposes of destruction. At least one of them, Frederick Soddy, of Oxford, who had won a Nobel prize for his researches into the phenomena of radioactivity, became so concerned with the appalling prospects of what would happen to a world whose people could not agree how to divide the abundant benefits available from the utilisation of enormous supplies of fossil fuel when atomic energy was tapped, that he deserted physical science and set out on a forlorn quest to convince a heedless mankind of the dangers with which it would one day be faced—"laying himself open", to use his own words, "to the abuse which passes for argument in matters that affect the pocket rather than the mind or soul".

Soddy had about as much success as Noah, and it is fair to say that his scientific colleagues resented his incursion into economics as much as did the economists. It is interesting now to read the prophetic words he wrote over twenty years ago about the discovery of the means of obtaining atomic energy. "If the discovery were made tomorrow there is not a nation that would not throw itself heart and soul into the task of applying it to war."

The magnitude of the tragedy for science that this, the most important scientific discovery ever made, with its triumphant verification of scientific prediction and all its promise for the expansion of human life and happiness, should have been made in time of war under the cloak of war secrecy, and used, not for the exaltation of life, but for its destruction, cannot be overestimated. The stupendous realisation that not merely in the remote stars, like the sun from which all our energy has been previously drawn, but at our very feet are stores of energy a million times greater than any we have yet known, has, as yet, passed the common man by. He can only look at the event not as the presentation to him of a choice between the use of atomic fire for the purposes of life or for destruction, but as nothing but a threat to his very existence. There is no wonder that for him atomic energy is synonymous with annihilation, nor that he should seek to prevent any race to produce bigger and better atomic bombs, and the free exchange of the results of nuclear chemists and physicists which could, in his opinion, lead to it.

To the scientists, however, the real shock was the clear recognition of just how far the misuse of the greatest gifts of science had taken man along the road to complete disaster. What had started with the introduction of poison gas into warfare in 1915 had led to a perversion of the real purposes of science so complete that even yet, with hostilities long past, military secrecy still demands silence on some of the greatest discoveries of science.

The scientist, who, in defence of his free science, and his very all, willingly endured the secrecy imposed on him by war is now vitally concerned lest science become permanently enmeshed in a web of secrecy. Against such a disaster we have the right as scientists to tell the citizens of the world of which we too are citizens, that secrecy and science are as the poles apart; that secrecy poisons the very spirit of science; that the real purpose of science is the bringing of Nature's secrets into the light of day; and that failure to free science in times of peace from the secrecy it accepted as a necessity of war will lead inevitably to

the blotting-out of all the fair prospect of a civilisation beside which "the triumphs of our times would appear tawdry, and our struggles for energy as a horrid dream".

If we claim that right, however, let us remember that inevitably we shall be called upon to justify it. We shall be told, and are being told, that free disclosure of all the results of science, without thought of the uses to which the advancement of natural knowledge is to be put, would jeopardise national security. To that we must answer that the brotherhood of science is international, not national; that science is for all humanity, not for single nations; and that the fruits of science are for life and living, not for destruction. The history of Germany in the last fifteen years has shown only too clearly how the enslavement of science in secret preparation for the destruction of other peoples leads inevitably to its own destruction.

Even as a matter of expediency, all military and industrial experience shows that, at best, the advantages secrecy confers are never permanent. At most, it enables nations or industrial concerns to keep only one jump ahead of their rivals. Secrecy begets secrecy and mistrust. It is like the cancer cells which start so much like healthy cells, but, in the end gnaw away the very vitals. I think that we here would agree that it is the secrecy imposed on the people of Europe's greatest nation at the present time that is so largely responsible for the mistrust of other nations. Democracy has had one bitter experience of secret preparation for war; and it is not for us, who are not charged with the tremendous responsibilities of national leadership, to dictate the actions that should be taken to guard against any possible secret preparations. But it is our right to deplore that secrecy, and to announce clearly and unmistakably to the world what we hold passionately to be true—that international brotherhood and peace can only come through the free and willing interchange of human ideas, and that not the least important factor in creating international co-operation and goodwill is the international community of science.

It has been the contention of all the great leaders of science that the pursuit of truth, without thought of the uses to which it may be put, is the first duty of science; but it is equally well recognised that the application of the results of such voyages of pure scientific discovery not only can, but often does, result in immense benefits to humanity, and the benefits are often far greater than those obtained by researches designed by the scientific planners. As Soddy puts it, "In scientific research nothing is less likely than that the discoverer will discover what he sets out to discover." . . . "Pasteur, studying optical isomerism, was led to the study of fermentation in passing on the road to the recognition of the part played by bacteria. But the most important part of his work was neither in brewing nor saccharimetry. It revolutionised surgery and to it countless millions owe their lives." Perkin, setting out to synthesise quinine, prepared the first coal-tar dye, and founded the great colour industry of today.

"Scientific discovery is a growth rather than a journey according to plan. The voyage may be west to discover the east, and it is through fog and dead reckoning to put places upon rather than to hit them off from a map." So clearly recognised is this principle that the most abstruse researches may eventually serve mankind and that the full flowering of scientific genius can only be attained where there is freedom to follow the search, wherever it leads, that even in industrial research organisations, where so much study of specific problems in restricted fields is demanded, the man with vision and inspiration is given his head.

You may ask now what we here should do to help preserve that freedom of science which has been responsible for so many benefits to this country. Let us recognise at the outset that the great nations of the world, with whom rests the disposition of nuclear science, will little note what we say or do here; but

we can play a part, small in itself, but none the less important in the firm re-establishment of the international community of science. Already Australian science has taken its place in the International Scientific Unions and in the United Nations' Educational, Scientific and Cultural Organisation, and it is not irrelevant to note here a report by Professor Noyes, President of the American Chemical Society, on the recent meetings of U.N.E.S.C.O. at Paris, in which he commented, "If all international groups could come to agreement as easily as the scientists, many of the problems of the world would be solved in short order".

Next, we should clearly recognise that freedom of science today demands something more than the free interchange between scientists of the results of scientific research, couched in the jargon of science, which is unintelligible, and therefore secret, to the layman. If we demand freedom for ourselves from the constraints of secrecy, then surely it is our duty to interpret the results we obtain as well as we are able, and as often as is necessary, into the common language of the layman, and so to prevent the charge that we keep our results secret from him.

During the past year we have had five popular science lectures delivered. We could increase the number. We could make more use of the radio and the newspapers. It goes without saying that those of us who lecture in educational institutions should do all in our power to impart to our students the ideals and real purposes of science, but even in these institutions we could do more. Scientists can influence the students of science they teach but they may never even meet those students of the humanities who later become leaders in the non-scientific community. Surely it is our duty to endeavour, with some type of popular interpretation of science, such as might be given in lunch-hour lectures, to develop in them at least some sympathy, understanding and respect for science and its high purposes.

We would do well to begin at once to present to our own people the other side of the picture that the unlocking of the secret of atomic energy presents to mankind—a realm of possibilities beyond the vision of even our most far-seeing scientists. Man's progress in the past has come from his mastery of the sources of energy. Already he has learned much about the mastery of atomic energy. Uranium-graphite piles are already a practical source of heat energy, and atomic energy will soon be adapted for large stationary power plant units. In the future the atomic energy units using practically pure uranium 235 or plutonium will be much more compact. On the material side the gains seem even more imposing at the present time. Nuclear chemistry has led to the synthesis of four new trans-uranium elements, neptunium (93), plutonium (94), americium (95), and curium (96) by transmutation reactions from uranium. Plutonium is at present by far the most important of these, for it can be used to make atomic bombs or atomic power plants according to man's will. At least one radioactive isotope for every element in the series from hydrogen to curium has now been made and radioactive isotopes of most of the important elements can be made in quantities. The possibilities for research in the realms of pure chemistry, biochemistry and biology with labelled "tracer atoms" are unlimited, and already there is a flood of results obtained by their use.

There is another way in which we could endeavour to report the results of science to the non-scientific citizen. We could seek to enlist into the membership of our Society citizens who are not scientists, but who, nevertheless, love truth for truth's sake and would be prepared to come into partnership with us in our Society, as a kind of secular arm. Such an expansion of our membership would be no novelty. In 1935, for example, numerous citizens of good standing, interested in the aims and objects of the Society, were invited to become members, and many accepted the invitation.

It does not need me to emphasise the importance of endeavouring to enlist into our Society all those novitiates in science who will soon become graduates and on whose shoulders some day will rest the scientific hopes of this community. At Philadelphia, Sir Henry Dale recalled that over 200 years ago Benjamin Franklin used to require from every candidate for admission to the earliest of American learned societies an affirmative answer to the question "Do you love truth for truth's sake, and will you endeavour impartially to find and receive it for yourself, and communicate it to others?" If we could imbue our young men with the spirit of that rule we should have little to fear for the future of science in this country, and when the time comes, to pass on to them the torch, with the words of Alfred Noyes—

"Take thou the splendour, carry it out of sight
Into the great age I must not know,
Into the great new realm I must not tread."

One of the great difficulties in the instillation of the real spirit of science into young men and women in this country is the lack of graduate schools. It is fair to say that it is at the universities and to a lesser extent, the technical colleges, that the spirit of free enquiry flourishes most vigorously. The longer the time our young men can spend in the atmosphere of such institutions, the greater should be their desire to seek truth for truth's sake. Some of our universities have recognised the deficiency and are now preparing to offer the Ph.D. degree. Two extra years of training and research and maturity should prove of infinite value. There are some difficulties to be met, such as the provision of finances and the dangers of inbreeding, but participation in some university teaching work, and the adoption of the practice obtaining in America, of strongly recommending students to attend a graduate school other than the school from which their first degree was obtained, could greatly strengthen science in Australia.

The value of the interchange of students and mature scholars, not only between Australian universities, but with educational and research institutions all over the world, cannot be over-emphasised. The best way of understanding other peoples and their problems is to live with them; and nothing makes a greater contribution to the international community of science than this friendly interchange of scientists. Lest any should fear that Australia could offer little to attract scientists from abroad on exchange, let me assure them that in America at least, particularly among the young men, I found not only willingness but even eagerness. It is true that Australia cannot offer such magnificent research facilities as some other countries, but a little intelligent scientific planning would greatly help. Let me make one suggestion. Every department of organic chemistry in Australia is more or less compelled to carry a large stock of organic chemicals. Each laboratory probably requires only a little of each of these, so that supplies are purchased in the worst markets. Because of our remoteness from the manufacturing countries it takes months to replenish exhausted stocks. If there were one central Australian store, maintained by the Government, whose purpose was to purchase in quantity at cheap prices and to carry a complete range of every chemical manufactured, many chemical research projects could be smoothly maintained instead of being interrupted, or, as often happens now, completely abandoned.

It is unthinkable that here in time of peace authority should ever demand concealment or distortion of any new scientific discovery. Nevertheless we must be on our guard to prevent it ever from happening. To that end it is of paramount importance that we should maintain and control some instrument of free publication. The members of this Society take pride in the long record of publication of our Journal, which is widely circulated to free scientific institutions

throughout the world. The results it records may not always be great or important, but they stand in their place to be freely used by all who desire. During this year it was suggested to the Council that the decision of the Council of Scientific and Industrial Research to publish an Australian journal of research would dispense with the need for a journal such as ours, and that soon, whether we liked it or not, lack of contributions would force us to cease publication. Nothing could be more catastrophic for free science in this country than such a result. Despite the obvious advantages of rapid publication and perhaps wider circulation, the danger of control of publication by a government department, whose policy can be rapidly altered by whatever political party is in power, are even more obvious. It was reassuring only a few days ago to read of Sir David Rivett's forthright declaration for scientific freedom, but Sir David Rivett will not always be Chairman of the Council for Scientific and Industrial Research.

I have tried to reproduce for you some of the important arguments put forward to us at Philadelphia by Sir Henry Dale, and to study the lessons they have for us here. I cannot do better in concluding them than to quote the actual words with which he closed his lecture there. Here they are :

“ It is not without significance that, whereas history, literature, art, and even religion all have national characters and local attachments, science alone of man's major intellectual interests, has no frontiers and no national varieties ; that science, like peace, is one and indivisible. And science, we should insist, better than any other discipline, can hold up to its students and followers an ideal of patient devotion to the search for objective truth, with vision unclouded by personal or political motive, not tolerating any lapse from precision, or neglect of any anomaly, fearing only prejudice and preconception, accepting Nature's answers humbly and with courage, and giving them to the world with unflinching fidelity. The world cannot afford to lose such a contribution to the moral framework of its civilisation, and science can continue to offer it only if science can remain free.”

THE ORBIT OF h 3494 (2^h 15^m·6, -35° 54' : 1900).

By HARLEY W. WOOD, M.Sc.,
Sydney Observatory.

Manuscript received, March 19, 1947. Read (in title only), April 2, 1947.

The motion of this double star was examined in 1931 by Finsen, who gave three sets of elements based on measures up to 1930. Measures since that time have departed more and more from the ephemerides corresponding to these orbits so that a recalculation seemed worthwhile.

The orbit was calculated by the method of Russell (1933) in the following steps :

(a) The observed values of position angle (p) and distance (d) were plotted separately as ordinates on squared paper with time in each case as abscissa. Smoothed curves adjusted to obey the law of areas were drawn among these points.

(b) Values of p and d were read from the graphs of step (a) and plotted as polar coordinates to obtain the Russell parameters of the apparent ellipse. On account of the restricted length of the observed arc a considerable range in the values of these parameters will represent ellipses following the curve to the accuracy expected. However, when an ephemeris is prepared each computed place, by plotting on the curve, can be made to yield a value of the periastron time (T) from the equation $T = M - t$, where t is estimated from the curve. The range of parameters is much reduced by the fact that the various values of T thus obtained should agree.

(c) The Thiele-Innes elements (see for example Aitken, 1935) were then computed and an ephemeris prepared from them for comparison with normal places derived from the curves of step (a). The residuals having been listed in order of the magnitudes of the coefficients in the equations of condition of the correction to one element, this correction was estimated—similarly for the other elements. This is easily done by dividing the list into groups in a way similar to that often used to obtain plate constants in photographic astronomy. A least square solution, frequently not warranted by the percentage accuracy of double star data, is thus avoided.

The normal places and the residuals O-C from the ephemeris of the adopted orbit are shown in Table 1. The third and fifth columns give respectively the residuals in position, angle and distance.

TABLE 1.
Normal Places.

Date.	p	O-C	d	O-C
1855	108°·7	-0°·1	1"·74	-0"·02
1885	80·1	+0·2	1·47	+0·03
1900	56·6	-0·5	1·13	-0·03
1920	5·5	+0·1	0·92	+0·02
1930	335·4	+0·1	0·95	-0·01
1935	322·2	-0·1	1·02	0·00
1945	300·9	-0·1	1·18	+0·01

TABLE 2.
Observations.

Date.	p (1900)	$O-C$	d	$O-C$	Nights.	Aperture.	Observer.
1837·91	122 ^o ·8	+0 ^o ·1	1 ^o ·58 (est)	-0 ^o ·19	3	18	h
52·82	110·2	-0·4	1·96	+·19	2-1	6·2	Jc
77·87	88·3	+0·3	1·54	-·01	2	11	Hwe, Stn.
87·94	75·6	-0·5	1·42	+·03	1	11·4	Pol
92·97	67·9	-1·1	1·19	-·11	2	11·4	Slr
97·10	65·8	+3·5	1·69	+·47	3	11·4	Slr
97·72	62·1	+0·9	1·28	+·08	1	24	See
1899·47	58·0	-0·1	1·07	-·10	3	24	Cog
1905·98	32·2	-12·3	1·20	+·15	2	26	Ol
09·77	31·8	-3·4	0·93	-·06	2	12	Ol
15·09	18·9	-1·4	0·96	+·03	4	9	V
17·01	14·0	-0·6	0·92	-·00	2	9	I
19·82	6·4	+0·4	0·88	-·04	4	17	δ
20·94	3·0	+0·5	0·90	-·01	3	17	δ
21·0	2·8	+0·5	0·96	+·05	2	9	I
22·92	356·2	-0·1	0·94	+·03	3	17	δ
24·82	351·1	+0·7	0·94	+·02	4	7·4	V
25·89	350·7	+3·5	0·80	-·12	3	26 $\frac{1}{2}$	ϕ
26·65	344·3	-0·7	0·90	-·03	4	7·4	V
28·64	338·2	-1·0	0·95	+·01	5	7·4	V
28·72	340·3	+1·4	0·90	-·05	4	7·4	tBr
28·82	338·6	-0·1	1·02	+·07	1	17	δ
28·87	333·7	-4·8	1·05	+·10	4	9	B
29·95	334·9	-0·6	0·92	-·04	4	26 $\frac{1}{2}$	B
30·02	335·5	+0·3	1·08	+·12	4	15	Wlq
30·69	333·4	-0·1	0·92	-·05	5	24	V
31·80	329·4	-1·1	0·92	-·06	4	26 $\frac{1}{2}$	B
31·96	329·3	-0·7	0·92	-·06	4	26 $\frac{1}{2}$	ϕ
32·59	328·0	-0·4	0·90	-·09	4	24	V
32·60	325·8	-2·6	1·02	+·03	3	17	δ
33·90	324·8	-0·2	0·96	-·05	4	26 $\frac{1}{2}$	B
34·61	323·2	-0·1	1·02	-·00	8	26 $\frac{1}{2}$	ϕ
34·63	324·3	+1·1	1·04	+·02	3	17	δ
34·96	321·4	-1·0	0·97	-·05	4	26 $\frac{1}{2}$	B
35·62	320·5	-0·4	1·08	+·05	4	24	V
36·93	317·9	+0·2	1·04	-·01	2	26 $\frac{1}{2}$	ϕ
37·12	316·9	-0·4	0·99	-·07	4	15	Smn
38·13	315·9	+0·9	1·03	-·04	4	26 $\frac{1}{2}$	B
38·67	314·1	+0·3	1·05	-·03	3	24	V
38·97	314·0	+0·9	1·11	+·03	1	26 $\frac{1}{2}$	ϕ
42·63	305·4	-0·1	1·16	+·02	4	15	V
44·67	301·3	-0·3	1·12	-·05	4	24	V
44·74	302·4	+1·0	1·10	-·07	4	26 $\frac{1}{2}$	B
46·69	296·7	-1·2	1·36	+·17	8	11·4	Wood
1946·92	297·5	0·0	1·25	+·05	4	9	Stromlo

Table 2 gives the observations and comparison with computed places. Columns 1 to 5 are as for Table 1, and the remaining ones give the number of nights, the aperture of the telescope in inches, and the observer. I am much indebted to Dr. W. H. van den Bos for sending me a copy of measures from his card catalogue at the Union Observatory, Johannesburg, and to Dr. J. G. Voûte for measures made at the Bosscha Observatory, Lembang, and to Dr. R. v. d. R. Woolley for the Stromlo measure. So far as they were available to me, the original publications were examined and in the case of Sydney measures the original observation books. The only points worthy of remark are that the 1877·87 measure has been given the weight of two nights since although the measures were made on one night it is the mean of two by different observers

and for 1892·97 one Sydney measure, made on a night noted as very poor, has been rejected.

The elements, still based on a somewhat inadequate arc, are as follows :

P .. 250 years,	Ω .. $100^{\circ}\cdot7$,	A .. $+1''\cdot119$,
n .. $-1^{\circ}\cdot439$,	ω .. $122^{\circ}\cdot4$,	B .. $-0''\cdot646$,
T .. 1931·95,	i .. $137^{\circ}\cdot5$,	F .. $-0''\cdot364$,
e .. $0\cdot24$,		G .. $-1''\cdot420$,
a .. $1''\cdot57$		

and the corresponding ephemeris :

Date.	p	d	Date.	p	d
1945	$301^{\circ}\cdot0$	$1''\cdot17$	1970	$263^{\circ}\cdot1$	$1''\cdot38$
1950	$292\cdot2$	$1\cdot24$	1975	$256\cdot4$	$1\cdot38$
1955	$284\cdot3$	$1\cdot29$	1980	$249\cdot7$	$1\cdot38$
1960	$276\cdot9$	$1\cdot33$	1985	$243\cdot0$	$1\cdot37$
1965	$269\cdot9$	$1\cdot36$	1990	$236\cdot2$	$1\cdot36$

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DIMENSIONAL METHODS IN THE DESIGN OF INDUSTRIAL CHEMICAL RESEARCH.

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THE NATURE OF INDUSTRIAL CHEMICAL RESEARCH.

The number of commercial firms engaged in manufacture, and in particular in chemical manufacture, which support what are referred to as research departments has increased all over the world in the last two decades and now constitute an appreciable proportion of the total scientific effort of any particular country. The question may well be asked as to what is the nature of the work done by such departments. I think it is fair to claim that much of the so-called industrial research might better be termed developmental work or the practice of adapting known physical and chemical principles to the attainment of economic ends. There is a great difference between showing that a certain desirable chemical product can be produced in the laboratory as a result of a certain chemical reaction and the design of a plant to carry out that reaction on a factory scale. Whether the discovery of the original reaction or the design of the final plant is the more laudatory achievement is a point on which the industrialist and the pure scientist will never agree; but whereas basic physico-chemical theory provides a guide to the attainment of new discoveries, there is no corresponding theory for the design of developmental research. The method adopted is almost entirely one of trial and error.

The "industrial research chemist" repeats the original experiment in terms of the description in the chemical literature and checks the experimental working conditions for optimum yield. He then repeats the experiment on a slightly larger (the so-called sub-pilot) scale and redetermines all the experimental parameters. Usually they are all found to be slightly different from those of the experiment on the laboratory scale. From the results of the sub-pilot scale plant he designs a larger or pilot scale plant and redetermines his working conditions. From these factors he may design the larger or factory scale plant.

At each change in scale there is, usually, an apparent change in the optimum working conditions often not attributable to any error in the experiments on the smaller scale. That there is such a progressive change in the optimum working conditions is simply accepted and practically no attempt has been made to explain why such a change should occur or whether there is a more efficient way of designing factory scale plant from reaction characteristics. One of the objects of this paper is to inquire how we should go about looking for such a more efficient method.

THE POSITION WITH REGARD TO OTHER SCIENCES.

The problem of designing effective large scale equipment from the performance of small equipment is by no means a problem peculiar to industrial chemistry, but is one which has been faced in many branches of applied science such as hydraulics, aerodynamics, ship building, structural engineering and more recently in the design of heat transfer equipment. In each case the problem is one of the dimensions of the variables concerned.

Consider a full scale bridge and a model at, say, one-tenth scale, geometrically similar and constructed from the same material. Consider any particular member of the model. Its volume, and therefore its weight, is one-thousandth that of the full scale or prototype, while its strength, depending on the cross-sectional area, is only one-hundredth that of the prototype. To make the model and prototype dynamically similar, or similar with respect to the balance of forces, it would be necessary either to make the model from denser material or material of lower yield stress. If the two bridges are dynamically similar, then the ratio

$$\frac{\text{Yield stress}}{\text{Density} \times \text{Acceleration due to gravity} \times \text{Linear scale}}$$

must be the same in both. This factor, as the reader may readily verify for himself, is one of zero physical dimensions.

The flow of fluids in two different sized vessels exhibits dynamical similarity when the quantity

$$\frac{\text{Velocity} \times \text{Linear dimension} \times \text{Density}}{\text{Viscosity}}$$

is the same in both vessels. This is also a quantity of zero dimensions and has been given the name Reynolds number.

Many similar examples could be given, and we may take it as a rule that the condition of dynamical similarity between two systems on different scales is determined by the equality of certain dimensionless quantities describing the state of the systems; and that only when the state of a system is described by equation between dimensionless quantities is it expressed in a form independent of its geometrical size.

The various quantities used to describe the state of a physico-chemical system include: flow rate, temperature, rate constant, equilibrium constant, pressure, space velocity, space time yield. None of these quantities is dimensionless. Indeed rate and equilibrium constants are properties so badly defined that they have different physical dimensions for each different order of chemical reaction. In consequence, therefore, when the industrial chemist expresses the results of an investigation into the possibilities of a certain reaction in the form of a functional relationship between, say, temperature, space velocity and space-time yield, he, by the use of non-dimensionless quantities, obtains empirical expressions which involve dimensional constants, themselves a function of undetermined variables including the geometrical scale of the equipment used. Accordingly the empirical "constants" may be expected to be different in each different sized apparatus. One of the first tasks of dimensional methods in industrial chemistry is to express the results of an investigation in such a form that the results are equally applicable to small or large scale equipment. This we can do if we find the means for setting up a condition of chemical similarity between reactions in different sized vessels.

ATTEMPTS TO SET UP THE CONDITIONS FOR CHEMICAL SIMILARITY.

A theoretical basis for a theory of chemical similarity was given in 1936 by G. Damköhler (1936). He took as fundamental axioms the conservation of mass, energy and momentum and wrote down these expressions in vector form for an elementary volume in a chemical system. He then took as his dimensionless parameters the ratios of all pairs of terms in the resultant set of equations (this is standard practice) and obtained five such quantities. He claimed that two chemical systems on different scales would be chemically similar if these five dimensionless quantities each have the same value in the two scales. Damköhler found that simultaneous satisfaction of these five conditions was only possible in a few special instances.

Edgeworth Johnston (1939) has discussed this work of Damköhler and has pointed out that in his general equations Damköhler has too many variables; he has ignored the necessary relationship between reaction rate and temperature and also he has not taken into account the fact that the boundary conditions for the energy equation can be adjusted independently of the scale by means of lagging or adiabatic jackets.

Laupichler (1938) has attacked the problem in a somewhat different manner. Working on the water gas exchange reaction, he obtained an expression for the overall chemical driving force and for the overall rate. The quotient of these two he calls the chemical resistance. This resistance he splits into two parts in series; a transfer resistance and a thermal resistance. The value of each of these resistances can then be evaluated in terms of the physical properties of the system. The performance of a large scale system can then be calculated from the resistance terms. The method of Laupichler has been extended by Hurt (1944).

THE VARIABLES CONCERNED.

In presenting the physical problem exhibited by a change of scale of a chemical system we shall proceed on a generalized method based on the treatment of Damköhler. The first step is to decide what variables are necessary in order to specify the system. We shall consider first a homogeneous system involving m different molecular species. From the phase rule we know that $m + 1$ variables are necessary in order to fix the state of such a system. The following quantities will therefore fix the state of the system:

- (a) The concentration of the molecular species ($m - 1$ variables).
- (b) The energy or the entropy (1 variable); and
- (c) The pressure (1 variable).

Let the atomic species in the system be denoted by A_1, A_2, \dots, A_a , a in number. Let n_{ij} represent the number of atoms of type i in molecules of type j , i.e. the molecule B_j may be represented as

$$B_j = n_{1j}A_1 n_{2j}A_2 \dots$$

Let ν_j molecules of type j enter the chemical reaction, which thus may be represented by:

$$\sum \nu_j B_j = 0$$

or

$$\sum \nu_j (\prod_i n_{ij} A_i) = 0 \dots \dots \dots (1)$$

Let C_j be the number of grammolecules of type j in unit volume.

If any small element of volume is taken in a continuous reactor, values may be assigned to the controlling properties in that element at any instant. The values will, however, in general change as the element proceeds along the stream. The various factors which produce this change include:

- (a) Change due to chemical reaction, changing the molecular concentration, the energy, the volume, and therefore the linear velocity.
- (b) Changes produced by the stream.
- (c) Changes produced by diffusion across the stream.
- (d) Changes produced by long-hop processes such as low pressure effusion or thermal radiation, or transfer of momentum by sound waves.

Let:

k be the velocity of the reaction in gramme equivalents per unit volume per unit time.

v be the stream velocity in units of length per unit time.

D_j be the diffusion coefficient for the j th component in units of length squared per unit time.

The equation for the conservation of mass then takes the form :

$$\frac{\partial C_j}{\partial t} = -v_j k - \text{div}(\mathbf{v}C_j) + \text{div}(D_j \text{ grad } C_j) \dots\dots\dots (2)$$

where there is no transport by a long-hop process. There are m equations of this type. In these equations $\frac{\partial C_j}{\partial t}$ represents the rate of change in the concentration of component j at some fixed point in the reactor, $v_j k$ represents the rate of destruction of component j per unit volume as a result of chemical reaction, $\text{div}(\mathbf{v}C_j)$ represents the net rate of increase in the concentration as the result of more component j streaming into unit volume surrounding the point under consideration than that streaming out, while $\text{div}(D_j \text{ grad } C_j)$ represents the rate of accumulation at the point consequent upon diffusion of j . The operation div and grad both represent vector differentiations with respect to the distance, div operating on vector quantities represented by clarendon type and grad on scalar represented by italics. Consequently we can write

$$\text{div}(\mathbf{v}C_j) = \mathbf{v}(\text{grad } C_j) + C_j(\text{div } \mathbf{v}).$$

The divergence of \mathbf{v} or the rate at which the velocity changes as a combined result of streaming and the chemical reaction is related to the volume change (ΔV) (in units of volume per gramme equivalent reacting) by the expression

$$\text{div } \mathbf{v} = k \Delta V.$$

Under steady state conditions $\frac{\partial C_j}{\partial t}$ in equation (2) is zero and we have

$$0 = -v_j k - \mathbf{v} \text{ div } C_j - C_j k \Delta V + \text{div}(D_j \text{ grad } C_j) \dots\dots\dots (3)$$

On combining these physical equations with the one for the chemical reaction we get in all $m+1$ equations in $3m+ma+3$ variables equivalent to one equation in $2m+ma+3$ variables and involving $2m+ma+1$ terms. If every term is to have the same dimensions, then it follows that the ratio of any pair of terms is an expression with zero dimensions. There are $2m+ma$ such independent ratios, and therefore $2m+ma$ independent equations in the $2m+ma+3$ variables. The dimensions of three independent variables may therefore be chosen independently. The independent variables may be most conveniently taken as those of mass (m), length (L) and time (t). The dimensions of the variables in equation (3) therefore are :

- v_j .. 0
- k .. $mL^{-3}t^{-1}$
- \mathbf{v} .. Lt^{-1}
- div and grad both L^{-1}
- C_j .. mL^{-3}
- ΔV .. $m^{-1}L^3$
- and D_j .. L^2t^{-1} .

So that every term in equation (2) has dimensions $mL^{-3}t^{-1}$.

Pressure is a measure of the rate of change of momentum across a surface. Thus if we specify the momentum flow across the surface we have fixed the pressure. For the equation of conservation of momentum of our system we may write

$$\frac{\rho \partial \mathbf{v}}{\partial t} = -\rho(\mathbf{v} \cdot \nabla)\mathbf{v} - \text{grad } p + \rho \mathbf{v} k \Delta V + \nu \rho (\nabla^2 \mathbf{v} + \frac{1}{3} \text{ grad div } \mathbf{v}) \dots\dots\dots (4)$$

Where

- ρ is the density of the stream,
- p is the pressure, and
- ν is the kinematic viscosity.

In equation (4) $\rho \frac{\partial \mathbf{v}}{\partial t}$ represents the total rate of momentum change per unit volume at a fixed point in the reactor and the various terms on the right-hand side represent the forces acting per unit volume; $\rho(\mathbf{v} \cdot \nabla \mathbf{v})$ as a result of the excess of momentum carried per unit time into, over that carried out of unit volume by the stream, $\text{grad } p$ as a result of external forces, $\rho \mathbf{v} k \Delta V$ as a consequence of the volumetric expansion produced by the chemical reaction, $\nu \rho \nabla^2 \mathbf{v}$, as a result of the friction forces produced by (ordinary) viscosity and $\frac{1}{3} \nu \rho \text{grad div } \mathbf{v}$ as a result of frictional forces produced by the viscosity of compression. (Brillouin, 1907.) Under steady state conditions $\frac{\partial \mathbf{v}}{\partial t} = 0$, and we write

$$0 = -(\mathbf{v} \cdot \nabla) \mathbf{v} - \frac{1}{\rho} \text{grad } p + \mathbf{v} k \Delta V + \nu (\nabla^2 \mathbf{v} + \frac{1}{3} \text{grad div } \mathbf{v}) \dots \dots \dots (5)$$

There is only one equation (5) having six variables and four terms. There are therefore three independent dimensions which again may be taken as m, L and t. We have, then, for the dimensions of ρ , p and ν

ρ mL⁻³
 p mL⁻¹t⁻²
 and ν L²t⁻¹.

So that every term in equation (4) has dimensions mL⁻²t⁻².

For the equation of conservation of energy we have :

$$\frac{\partial}{\partial t}(c_p \rho \theta) = -\text{div}(c_p \rho \theta \mathbf{v}) + Qk + J \mathbf{v} \text{ grad } p + \lambda \nabla^2 \theta + \frac{4\alpha}{i} \sigma T^3 \theta \dots \dots \dots (6)$$

where :

- Q is the heat evolved by the reaction in units of energy per gramme equivalent. For an isopiestic system $Q = -\Delta H$.
- c_p is the specific heat of the reaction mixture at constant pressure.
- λ is the thermal conductivity of the reaction mixture.
- ρ is its density.
- T is absolute temperature of the walls of the reaction vessel, assumed uniform.
- θ is the temperature of the point under consideration in excess of wall temperature.
- α is the relative emissivity of the reaction mixture.
- σ is the Stefan-Boltzmann constant.
- i is the ratio of the volume to the surface area of the reaction vessel, and
- J is Joule's equivalent.

In equation (6) $\frac{\partial}{\partial t}(c_p \rho \theta)$ is the change in thermal energy per unit volume at any point in the reactor, $\text{div}(c_p \rho \theta \mathbf{v})$ is the excess thermal energy carried into unit volume by the stream, Qk the heat generated per unit volume by the stream, $J \mathbf{v} \text{ grad } p$ is the heat generated per unit volume by friction, $\lambda \nabla^2 \theta$ is the heat transferred per unit volume by thermal conductivity, and $\frac{4\alpha}{i} \sigma T^3 \theta$ is the heat transferred per unit volume by radiation, all measured per unit time. The last term is accurate only under conditions for which the vessel of reaction mixture does not absorb the thermal radiation too strongly and all portions of the vessel are effectively exposed to wall radiation of the same intensity. The internal walls are effectively black, so that the radiation emitted per unit area per unit

time is σT^4 . Of this a fraction α is absorbed by the gas, so that the amount of wall radiation absorbed by any unit volume of gas in unit time is equal to

$$\alpha\sigma T^4 \frac{\text{Area of walls}}{\text{Volume of reactor}}$$

The ratio Volume/Area we have written as i . For any form of cylindrical reactor i is also the ratio Surface area/Perimeter and may thus be referred to as the hydraulic radius of the reactor (for a circular cylinder i is half the radius). The amount of thermal radiation per unit time sent by unit volume of gas to the walls is clearly

$$\frac{\alpha}{i}\sigma(T+\theta)^4,$$

where θ is the excess temperature of the point under consideration. As long as θ/T may be regarded as a small quantity the net heat loss per unit area per unit time due to radiation is clearly

$$\frac{4\alpha}{i}\sigma T^3\theta.$$

Under steady state conditions the left-hand side of equation (6) vanishes and the equation for conservation of energy may be written

$$0 = -C_p \rho v \cdot \text{grad } \theta - c_p \rho \theta k \text{ div } v + Qk + Jv \cdot \text{grad } p + \lambda \nabla^2 \theta + \frac{4\alpha}{i} \sigma T^3 \theta \tag{7}$$

There is only one equation (7) with six terms and nine dimensional variables. Consequently there are four independent dimensions which may be taken as m, L, t and θ (the temperature). In terms of these the dimensions of the variables are :

c_p	$L^2 t^{-2} \theta^{-1}$
θ and T	θ
Q	$L^2 t^{-2}$
J and α	0
λ	$m L t^{-3} \theta^{-1}$
σ	$m t^{-3} \theta^{-4}$ and
i	L .

So that every term in equation (6) is of dimensions $m L^{-1} t^{-3}$.

From the ratio of pairs of terms in equations (3), equation (5) and equation (7) we may derive, after the method of Damköhler, all the dimensionless parameters concerned in the statement of the complete similarity of two different chemical systems. We may, without serious loss of industrial generality, restrict our studies at this point to long circular cylindrical reactors of radius R and length l .

From the mass equation we may derive three dimensionless ratios, viz. :

$$\frac{v_j k}{v \text{ div } C_j} \quad \text{or} \quad \frac{v_j k l}{v C_j} \tag{I}$$

$\text{div } C_j$ being taken as dimensionally equivalent to C_j/l .

$$\frac{v_j k}{D_j \nabla^2 C_j} \quad \text{or} \quad \frac{v_j k R^2}{D_j C_j} \tag{II}$$

and

$$\frac{v \text{ div } C_j}{C_j k \Delta V} \quad \text{or} \quad \frac{v}{k l \Delta V} \tag{III}$$

In the momentum and energy equations we shall ignore the terms in $\text{grad } p$, which in all usual chemical systems will be small. From the momentum equation

we obtain two dimensionless expressions, one of which is identical with III above. The other is the well-known Reynolds number,

$$\frac{\mathbf{v} \text{ grad } \mathbf{v}}{\nu(\Delta^2 \mathbf{v} + \frac{1}{3} \text{ grad div } \mathbf{v})} \quad \text{or} \quad \frac{\mathbf{v}R}{\nu} \dots\dots\dots \text{IV}$$

From the energy equation three dimensionless ratios are obtained, one of which is the well known Peclet number, viz. :

$$\frac{\text{div}(\theta c_p \rho \mathbf{v})}{\lambda \text{ div grad } \theta} \quad \text{or} \quad \frac{c_p \rho \mathbf{v}R}{\lambda} \dots\dots\dots \text{V}$$

The other two constitute the condition for thermodynamical similarity,

$$\frac{Qk}{\lambda \nabla^2 \theta} \quad \text{or} \quad \frac{QkR^2}{\lambda \theta} \dots\dots\dots \text{VI}$$

and the condition for radiative similarity, viz. :

$$\frac{Qk}{\theta(8\alpha R^{-1} \sigma T^3 - c_p \rho k \Delta V)} \dots\dots\dots \text{VII}$$

in which i has been taken as $\frac{1}{2}R$.

These seven dimensionless quantities are capable of giving a description of any homogeneous chemical system which is independent of the scale of the vessel in which the reaction is carried out. In many cases only some of these quantities need be considered. Thus unless the reaction mixture is very opaque and also the temperature is excessively high the condition for radiative similarity may be neglected and VII becomes equivalent to III, V and VII. If in addition the reaction is approximately isometric, condition III may be ignored. Further if the flow in the reactor is laminar, condition IV may probably be neglected. If the flow is turbulent, both D_j and λ are functions of \mathbf{v} .

THE CONDITIONS FOR SIMILARITY IN MODEL AND PROTOTYPE.

If a condition of similarity between a chemical system in a model vessel and one in a large scale or prototype is to be attained, then all seven dimensionless ratios I to VI must have the same value in both vessels. We will consider the case in which the same reaction is studied in both vessels. In doing this we do not exclude the possibility of attaining similarity between two different chemical reactions or between a chemical and a physical reaction such as would be implied by the setting up of the equivalent electrical circuits. We chose the same reaction mixture as the easiest way of attaining similarity with respect to all alternative chemical reactions.

We now have in conditions I to VI equality of the factors $\nu_j, C_j, D_j, \Delta V, \rho, c_p, Q, \lambda, \alpha, \sigma$, on the two scales. Conditions of similarity then become

I and III .. $\frac{k l}{\nu} = \text{Const.}$

II .. $k R^2 = \text{Const.}$

V and IV .. $\mathbf{v} R = \text{Const.}$

VI .. $\frac{k R^2}{\theta} = \text{Const.}$

VII .. $\frac{k R}{T^3} = \text{Const.}$

Now if the output is increased n -fold we have

$$\mathbf{v}_h R_h^2 = n \mathbf{v}_m R_m^2$$

where the subscript $_h$ refers to the full scale vessel and the subscript $_m$ refers to the model.

Combining these conditions above we see that

$$R_h = nR_m$$

$$v_h = \frac{1}{n} v_m$$

$$l_h = nl_m$$

$$k_h = \frac{1}{n^2} k_m$$

$$T_h = 3 \frac{1}{\sqrt{n}} T_m$$

Since the relationship between k_h and k_m (for homogeneous reactions at fixed pressure) also involves a relationship between T_h and T_m , viz.

$$e^{-\frac{b}{T_h}} = \frac{1}{n^2} e^{-\frac{b}{T_m}}$$

a condition of geometrical similarity with respect to the differential equations above can only be set up with one possible scale change and in most cases that change is very small. Take as a typical example $b=4,000$ and $T_h=800$. The allowed value of n then becomes 2.0 and n is less still if b/T_h is larger than 5. Thus the conditions for the attainment of complete similarity are not particularly useful if the same reaction is to be maintained on both scales. Thought must therefore be given to the usefulness of conditions of partial similarity (all the dimensionless parameters given above are not equally important in determining the efficiency of the chemical reaction, and under certain circumstances some may well be eliminated from practical considerations). Alternatively we may consider systems in which different reactions are used on the two scales. Two rules appear to emerge from the analysis above. *For combined reaction-kinetic and dynamical similarity it is necessary both that the flow rate and the chemical reaction rate should both be faster on the smaller scale reactor.*

More scope for the exploration of the method of chemical similarity is given by heterogeneous reactions. But again complete similarity demands embarrassing properties for the model system if the change in scale is large. Thus in general the catalyst grains in the model vessel should be larger than those in the full scale vessel and the catalyst activity higher on the smaller scale consonant with our finding above that the smaller scale reaction should be faster. It appears, therefore, that this subject is one requiring considerable detailed research before any great progress can be attained. A certain amount of progress is possible, however, by exploring the significance of some of the dimensionless ratios given above.

SIGNIFICANCE OF THE DIMENSIONLESS RATIOS.

The number I given in section (4) above is the ratio of the average life of a molecule under the conditions of the reaction to the average time taken to flow through the reaction vessel. The number II is the ratio of the average life of the molecules to the average time taken to diffuse across the reactor. I is obviously an expression for the efficiency of the reaction, II not so obviously. But whereas we may specify the average time of passage of the reaction vessel it is obvious that the molecule will spend different times in the reaction zone according to its distance from the wall and a complete description of the state of the system requires not only that we specify the average time of transit but also that we give the population curve, or frequency distribution curve from the reaction times (Bosworth, 1947). In the absence of diffusion the population

curves are easy to derive. In laminar flow the curve is that of an inverse cube, in turbulent flow roughly an inverse ninth power curve or more accurately

$$\frac{1-\tau^{-8}}{\tau^9}$$

The effect of diffusion, which is the more pronounced the smaller the radius of the reaction vessel, tends to distort these distribution curves tending finally towards the shape of a law of errors curve. The dimensionless number II is the factor which determines the shape of the distribution curve.

The dimensionless quantity III, which clearly is of importance only for systems of a non-isomeric nature, is a measure of the ratio of the volume swept through by the reaction mixture in unit time to the volume increase in unit time consequent on chemical reaction. III thus is a measure of the hydrodynamical acceleration produced by chemical reaction which for a given reaction taking place at a given rate depends only on the time taken in passage through the reaction zone, viz. l/v .

The condition for thermodynamical similarity (VI) is the ratio of the heat developed by the chemical reaction in unit time to the heat removed by conduction in unit time. Similarly the quantity VII is the ratio of the reaction heat in unit time to the heat removed in unit time by the combined effects of radiation and of the convection arising from the volume changes produced by the reaction. Radiation and this natural convection are similar only in respect to the changes consequent on changes in the geometrical dimensions of the reaction vessel. With respect to changes in temperature they are, of course, entirely different. Quantities VI and VII are accordingly those factors which determine the magnitude of the temperature differences across the reaction mixture. The quantity V, like II, determines the shape of a distribution curve, this time for the temperature difference across the reaction mixture.

Quantity IV, the Reynolds number, determines the flow pattern and, in the turbulent zone, the magnitude of D_j (for turbulent diffusion) and λ (for turbulent conduction of heat).

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GEOLOGY OF THE ASHFORD COALFIELD.

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With Plate I and one Text-figure.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION AND ACKNOWLEDGEMENTS.

The Ashford Coalfield is so named from its occurrence adjacent to the town of Ashford. The coal measures outcrop in a narrow discontinuous belt from the vicinity of Bonshaw, on the Queensland border, to the neighbourhood of Inverell, a distance of approximately 50 miles. Known exposures of coal are confined to the County of Arrawatta.

Mr. D. G. Moye, B.Sc., assisted me on this survey, and his able cooperation is hereby gratefully acknowledged. The coal analyses were made in the Departmental Laboratory under the direction of Mr. E. N. Reidy, Chief Analyst.

The field work was carried out in the latter part of 1945. The positions of the various geological boundaries were mostly sketched in relationship to the nearest portion, lease or road boundary or by pace traverses. The survey in the vicinity of the Ashford Coal Mine was made with a telescopic alidade and plane table. A detailed plan of this area is filed in the Geological Survey Branch of the Department of Mines, together with a plan of M.L.1, Parish of Hallam, showing the positions of the shafts in that locality.

TOPOGRAPHY AND ACCESS.

The area is principally one of low and medium relief and the rivers mostly flow in fairly broad open valleys. The rougher country is confined mainly to areas of granite, particularly in the northern section, and to a lesser extent to the Carboniferous sedimentary rocks. The coal measures generally occupy valleys between hills formed of the other rocks.

The river system comprises the MacIntyre River, the Severn River, which flows into the MacIntyre, Frazer's Creek and their tributaries. It was developed prior to the eruption of the Tertiary basalts and although modified by these flows, the valleys probably occur in approximately the same positions as in pre-basalt time. In the vicinity of Bukkulla, the MacIntyre River and Frazer's Creek change their courses from north to north-west. Some miles further on they swing back and again follow a northerly course. This bend is probably a reflection of a sharp swing in the trend of the country rocks or of cross-faulting.

The nearest railhead in New South Wales is Inverell, which is 509 miles from Sydney by rail and 1,912 feet above sea level. Access by road is good, the coal measures always being less than two miles from a main road and never very far from the main road between Inverell and Bonshaw. Several of the roads shown on the County of Arrawatta as crossing the area are not trafficable, but roads of access could easily be constructed to any point where coal is likely to be found in commercial quantities.

Geological Map
ASHFORD COALFIELD
County of Arrawatta

Geological Map ASHFORD COALFIELD County of Arrawatta

SCALE
MILES 0 2 4 6

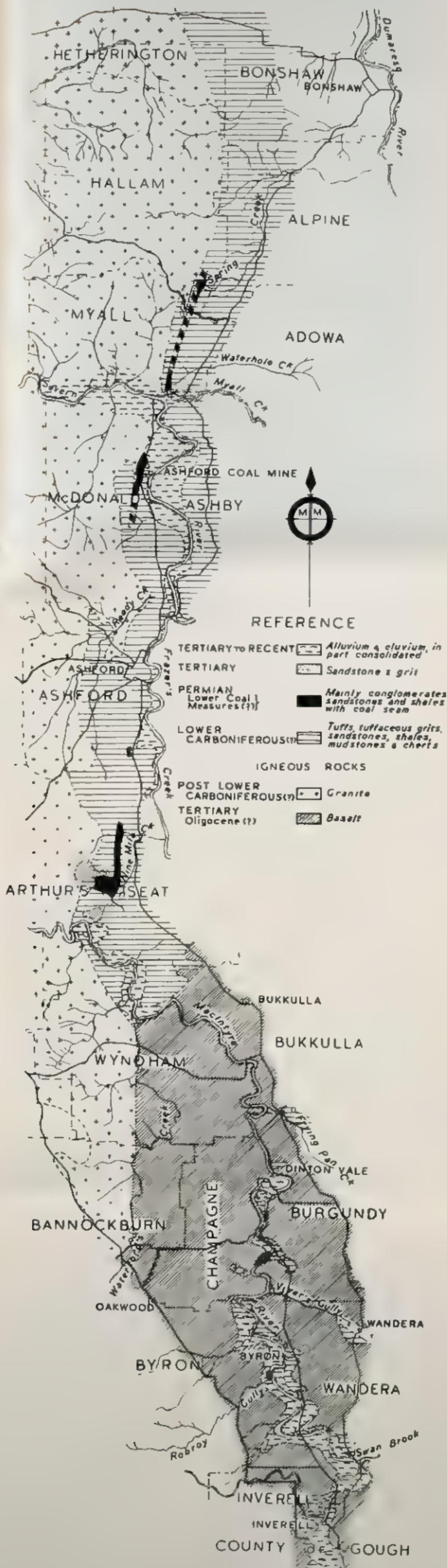


Figure 1.—Geology of the Ashford Coalfield.

GEOLOGY.

There have been numerous reports based on short visits to various parts of the Ashford Coalfield, but up to the present there has been no detailed geological survey of the whole field. David (1885) reported on coal at the site where the Ashford Coal Mine was subsequently opened. He also published a cross-section of the area in Memoir of the Geological Survey of N.S.W., Geology No. 4 (David, 1907). Pittman (1896) reported on parts of an area extending from south of the coal mine to the neighbourhood of Bonshaw. A report of a "Geological Reconnaissance of the Ashford Coalfield" was made by Jones in 1924.

The work described herein was confined, as far as possible, to tracing the limits of the Permian Coal Measures. Other rocks of the district were examined only in so far as was necessary to determine their general structure and relationships to the coal measures.

The geology of the district is shown in Figure 1. The rocks are now described, commencing with the sedimentary ones, taken in ascending stratigraphical order.

Carboniferous (?).

The oldest rocks in the district consist of a series of tuffs, tuffaceous grits, mudstones, shales, sandstones and cherts. These rocks were not mapped separately, but further work would probably disclose two main groups, one composed mainly of massive coarse tuffs with tuffaceous grits and sandstones, and another consisting mainly of thinly bedded mudstones, shales and cherts.

The rocks had been closely folded, probably faulted and subjected to considerable erosion prior to the deposition of the Permian Coal Measures. The strikes are mainly between N. 30° E. and N. 30° W. Dips measured are generally steep, varying from 30° to almost vertical, and in the large majority of cases are in an easterly direction, although in some places westerly dips are found.

Faulting of the sediments can be plainly seen in places, as for example along Spring Creek in the Parish of Alpine and along Reedy Creek in the Parish of McDonald. Whether the faults are pre- or post-coal measures it is impossible to say. Some at least must be post-coal measures, as the measures themselves show evidence of cross-faulting. The western boundary between the coal measures and the older sediments appears to be a faulted junction.

The age of these rocks has been the subject of much discussion, and the question cannot be regarded as finally settled. The only fossil evidence found during the survey was the cast of portion of a crinoid stem in the Parish of Ashford, adjacent to the town cemetery.

David (1893) and Pittman (1896) classified them as Carboniferous (Gympie). This classification was adhered to by them in a later report (David and Pittman, 1899), commenting on a paper by Dunn (1897). Jones (1924) also classified them as Carboniferous. Later David (1932) modified his views and placed the sediments in the Devonian. He was probably influenced in this decision by the similarity in lithology between these and the Barraba and Silverwood Series. The latter series outcrops across the border in Queensland, and has been described by Richards and Bryan (1924) as Devonian. David also regarded a belt of limestone about 10 miles north-west of Ashford as being Devonian and reported plant remains, considered by him to be *Lepidodendron* (?), from north of Bonshaw. Carey and Browne (1938) regarded these rocks as Devonian.

The Geological Survey of New South Wales has always considered the limestone to the west of Ashford as being Carboniferous. In 1940 Raggatt and others collected specimens of *Symplectophyllum mutatum* Hill (Raggatt, 1941), which Hill (1942) considers to be Upper Viséan in age. Upper Viséan fossils

have also been reported from the Texas-Bonshaw-Glen Lyon area of Queensland by Ball (1923), Bryan (1925) and Hill (1933, 1942).

In the absence of definite fossil evidence to the contrary, it is considered preferable not to change the view accepted previously by the Geological Survey as to the age of the older rocks of the Ashford Coalfield, especially as Carboniferous fossils are known to occur in nearby areas both on the New South Wales and Queensland sides of the border.

Carey and Browne (1938) consider that the Lower Kuttung and Upper Burindi Series are the Australian terrestrial and marine equivalents respectively of the European Viséan. They also consider that the pre-Permian rocks at Ashford were folded at the close of Burindi time during what they designate the Drummond movement and that there was no post-Upper Kuttung and pre-Permian orogeny in Queensland and New South Wales. The sediments in the Ashford district were heavily folded and subjected to considerable erosion prior to the deposition of the Permian Coal Measures, so this would place the end of Lower Carboniferous time as an upper limit to their deposition.

Permian.

Lower Coal Measures (?).

Pittman (1896), David (1907, 1932) and Jones (1924) regarded the Ashford Coal Measures as the equivalent of the Greta or Lower Coal Measures. Pittman (1896) records the occurrence of both *Gangamopteris* and *Glossopteris* in these beds.

The coal measures consist of a thin series of conglomerates, sandstones and shales containing a coal seam, which is up to 27 feet thick. They form a narrow discontinuous belt from Spring Gully in the Parish of Hallam, south-west of Bonshaw, at the northern end, to Byron, near Inverell, at the southern end.

The greatest width of outcrop measured was about 65 chains in the Parish of Arthur's Seat, between Ashford and Bukkulla. At this point the measures are apparently in the form of a syncline. This is the only locality from which easterly dips have been recorded in the coal measures.

The normal strike varies between N. and N. 30° E. with the dips westerly at between 30° and 40°. At Arrawatta, north of Inverell, a dip of about 55° in a direction N. 70° W. was recorded (Booker, 1941).

The greatest thickness of Permian sedimentary rocks measured was along the small gully described by Pittman (1896), about 70 chains south of the mine. Here they have a horizontal width of about 1,000 feet and dips measured varied between 30° and 35°. This would correspond to an actual thickness of the order of 550 feet. David (1930) quotes 510 feet as the thickness in the same locality. In the Cessnock-Greta and the Singleton districts the Greta Coal Measures are 200–250 feet thick. At Muswellbrook they are 645 feet thick (Raggatt, 1929), but the Skeletar Stage, which forms the lower 275 feet of the measures, is largely made up of rhyolite and rhyolite breccia, leaving 370 feet as the thickness of the sedimentary portion of the Lower Coal Measures. The development of an apparent thickness of 550 feet of Greta Coal Measures at Ashford, compared with 200–370 feet in the main areas of development, points to the possibility of either repetition due to faulting or the presence of Permian sediments other than Greta Coal Measures. Dunn (1897) refers to the occurrence of glacial conglomerate in the vicinity of the coal mine. This was refuted by David and Pittman (1899). However, David (1930) later reported the occurrence of glaciated pebbles from the same locality and was of the opinion that they may be referable to some part of the Upper Marine. Voisey (D.Sc. Thesis, unpublished) suggests that the Ashford sediments may be the terrestrial equivalents of Permian marine strata. It seems probable that the upper portion of the Permian at Ashford may be of Upper Marine age. If it could be definitely proved, it would preclude any

possibility of the Ashford Coal Measures being correlated with the Upper Coal Measures of the Newcastle district.

Coal has not been proved present at all points where the measures outcrop. However, as it has been proved at Spring Gully in the north and at Arrawatta in the south, and is 27 feet thick at the coal mine, it is reasonable to assume it will most likely be present wherever the measures outcrop.

The most northerly point of the area where coal has been proved is at Spring Creek in M.L.1, Parish of Hallam. Coal measures reputedly outcrop further north (Pittman, 1896), but the coal has not been proved. Two shafts have been sunk on the bank of Spring Creek. It was impossible to inspect either of the shafts which are at present in a state of disrepair. In the bank of the creek adjacent to the No. 1 or Old Shaft, the strike of the sediments appears to be about N. 40° W. and the direction of the dip S. 50° W. Near the No. 2 or Main Shaft the coal is not visible and the strike could not be determined. Further to the west the directions of dip of sediments, which probably form part of the coal measures, vary considerably. Due east along Spring Creek, at a point where the creek swings away to the north, the Carboniferous is faulted and it is possible that this faulting has affected the coal measures.

Along a tributary creek, south of Spring Creek, near the boundary of portions 11 and 12, Parish of Hallam, the coal measures are exposed and are bounded on the west by Carboniferous sediments. A chain or so further west the latter have been intruded by a tongue of granite.

It is probable that the coal measures extend in a general southerly direction from this locality, although no outcrops were seen until just north of Myall Creek. At this point coal measure conglomerate can be seen in the bank of Waterhole Creek.

There are no outcrops of the measures visible along Myall Creek, although outcrops of Carboniferous rocks are frequent. If the measures cross the creek the most likely spot for them to do so is the southern bend in portion 1, Parish of Ashby. Here the banks and bed of the creek are entirely in alluvial material.

It has been reported (Pittman, 1896) that after heavy floods on the Severn River, large masses of coal were found in the river adjacent to Frazer's Creek Homestead. It is probable, therefore, that the coal seam outcrops in the bed of the river, although it cannot be seen. The most likely position for the outcrop to occur is covered by a long and deep waterhole between portion 3, Parish of Ashby, and portion 1, Parish of McDonald.

The southern bank of the river is covered by alluvium and the coal measures are next found along and adjacent to T.S.R. 28,605, in the vicinity of the coal mine, which has been opened up by means of an inclined shaft. This is the only area in the coalfield where any actual reserves have been proved. Nine bores were sunk recently and the results appear to indicate that the thickness of the seam increases in a southerly direction and at the same time the quality declines. The No. 9 bore, which is the most northerly, shows a thickness of coal of 20 feet, No. 8 bore 23 feet, the inclined shaft 27 feet, No. 5 bore 26 feet, and No. 3 bore, the most southerly, 33 feet. A considerable proportion of the seam in No. 3 bore apparently consists of poor quality coal and bands of shaly material, so that the seam may be splitting and deteriorating towards the south. On the other hand, this bore is close to a presumed cross fault and there may have been a certain amount of repetition in the bore due to faulting. The thicknesses quoted have been calculated by assuming that the dip of the seam in all cases is constant at 35° and that the bores are truly vertical through the seam.

The average strike of the coal seam over the length of more than three-quarters of a mile proved in the bores is N. 6° E. The strike in the inclined shaft is N. 30° E. and the dip is N. 60° W. at about 40°. The coal seam is underlain by a bed of conglomerate of varying thickness and is close to the base

of the measures. The proximity to the eastern boundary between the coal measures and Carboniferous sediments should facilitate the location of sites for bores or shafts in any future prospecting operations.

In a creek about 70 chains south of the mine shaft there is a good outcrop of the coal measures striking N. to N. 25° E. and dipping to the west at from 30° to 35°, but the seam itself is not visible. About 30 chains north of the point where the creek crosses the roadway, the outcrop of the coal measures takes a sharp swing to the west and has probably been faulted.

South of the creek referred to above, the coal measures do not outcrop for some distance but probably continue in a southerly direction through a saddle in the divide between the creek and one further south.

There is a considerable break in the continuity of the coal measures adjacent to the township of Ashford. There are no recognizable outcrops from about five miles north to about three miles south of the town, where an isolated outcrop of typical Permian conglomerate is showing in the bed of a small creek adjacent to the Ashford-Inverell road. It is bounded on the east and west by Carboniferous rocks.

South of Ashford, in the neighbourhood of Nine Mile Creek, is one of the most interesting areas in the coalfield. The northern section of the outcrop consists of a narrow belt of sediments and shows typical westerly dips. The southern section is much broader and there are dips both to the east and west. The rocks consist mainly of conglomerates, shales and sandstones and are apparently in the form of a syncline which pitches to the north off the Carboniferous basement. The coal seam is probably present, although no coal was seen.

The next known outcrop of the coal measures is near Arrawatta, about 13 miles further south. The measures outcrop along the bed and western bank of the MacIntyre River in portions 1 and 17, Parish of Champagne. The outcrop was examined by Booker (1941) and the writer at a time when the level of the MacIntyre River was very low owing to a prevailing drought. The coal measures outcrop over a length of approximately half a mile and consist of conglomerates, clay shales containing abundant plant remains, and a coal seam. The seam had been prospected many years ago by a shaft, allegedly 45 feet deep, in portion 4, Parish of Champagne, but details of the results are not known. During the drought in 1941 when the coal measures in the bed of the river were exposed, the coal was prospected by means of a costean and a shaft. The coal was exposed in the costean over a distance of 15 feet, being equivalent to an actual thickness of 10 feet. The vertical shaft 13 feet deep, sunk on the seam, exposed the lower six feet. A sample of this section gave the following analysis :

Hygroscopic moisture	4.02%
Volatile matter	10.14%
Fixed carbon	70.80%
Ash	15.04%
No coke formed.					
Ash : Buff, flocculent.					

The coal is underlain by a bed of white clay, the exact thickness of which is not known. A sample of this clay was tested by firing at 1450° C. and formed a good white stoneware, approaching china body quality. Soon after the inspection in 1941 the outcrops and prospecting openings were submerged and have not been exposed since. It is possible that extensions of the coal measures may be found under the river alluvium and basalt, but any prospecting through the latter would be very expensive.

The only other outcrop of coal measures seen during the course of the survey was on the western bank of the MacIntyre River within the surveyed town of

Byron. An old map of the Parish of Byron, filed in the Geological Survey, shows coal outcropping in this vicinity, but no such outcrops were seen during the survey. The outcrop may have been noted at a time when the river was low and be submerged at the present time, as was the case at Arrawatta.

No outcrops of coal are known further south from the above. However, the area is apparently covered by basalt and a careful search of all creeks and gullies in the area, or the results of boring operations, may disclose further occurrences. The discovery of coal in this area would be important, both because of its proximity to rail and to the centre of the local demand at Inverell.

In most areas the coal measures are bounded on both the east and west by Carboniferous rocks. Along the eastern boundary the coal measures rest unconformably on the older rocks. The almost right-angled unconformity shows very well in Coal Gully adjacent to the coal mine shaft, and in the gully about 70 chains further south (see Plate I). At the latter site the gully runs parallel with the unconformable junction for about one chain.

The actual western boundary is not visible, but coal measures can be seen dipping westerly at about 30° within a chain of the Carboniferous rocks to the west. The most likely explanation is that the Carboniferous has been faulted against the coal measures. In the northern part of the Parish of Arthur's Seat and the southern part of the Parish of Ashford, the line of hills which is composed of Carboniferous rocks and represents the western and upthrow side of the fault is continuous between known outcrops of coal measures. Whether the fault is normal or overthrust is open to debate. The western boundary between the Carboniferous and coal measures in portion 58, Parish of Arthur's Seat, appears to be convex to the east between the tributaries of Nine Mile Creek, the Carboniferous rocks consisting partly of brecciated material. This would mean that the fault dips westerly and the fault would be an overthrust. However, in the absence of other confirmatory evidence it is impossible to be dogmatic. It is also noteworthy that there are several post-coal measure dykes of trachytic material in this locality, and the breccia may, at least in part, have resulted from this igneous activity.

The cross-faulting, referred to above, south of the mine, probably post-dates the fault forming the western boundary of the measures. The location has probably been influenced by the position of the tongue of granite which ends at the line of the fault.

The Ashford coal is much lower in volatile matter than other New South Wales Permian coals, the percentage varying between 10 and 25. It breaks up into small lenticular fragments and is considerably slickensided in places. Portions of the seam have a dull semi-coked appearance. Its nature infers alteration by considerable pressure and/or by adjacent igneous intrusions. The faulted western boundary of the coal measures proves that there has been considerable movement (and, if in the nature of an overthrust, considerable pressures developed) subsequent to the deposition of the coal measures.

Tertiary to Recent.

The deposits consist mainly of alluvium and eluvium, in part consolidated. They are very widespread throughout the area, although their depth is usually shallow and the mantle of weathered material would not exceed five to 10 feet in thickness in most instances. It is unfortunate that the nature of certain critical formation boundaries has to be inferred because they are obscured.

The different rock formations generally give rise to characteristic soils. The granites produce poor sandy soils, the basalts black, rich, clayey loams, which are so well developed around Inverell, and the Carboniferous sediments (locally known as "trap") form light-coloured loams. The soil derived from the coal

measures is least characteristic of all, being rather more sandy than those derived from the Carboniferous rocks and less sandy than those derived from the granites.

There is a small outcrop of sandstone and grit adjacent to the main Inverell-Bonshaw road, about half a mile north-west of Bukkulla. It was shown by David on an old parish map in the files of the Geological Survey as being of Tertiary age. Whether this determination was based on fossil evidence is not known. The outcrop was not examined in detail during the course of the present survey.

The Tertiary basalts are discussed below under the section on igneous rocks.

Igneous Rocks.

Granites.

The whole of the western margin of the area surveyed is occupied by granite. Two different types were collected. One, which in hand specimen closely resembles the tin granites of the New England, is pale-coloured and markedly porphyritic. Macroscopic examination shows that it consists of large phenocrysts of orthoclase and medium-sized phenocrysts of quartz in a groundmass of quartz, orthoclase, plagioclase, biotite and muscovite. The other is yellowish-pink in colour and much finer grained. There are no phenocrysts of orthoclase, although small quartz phenocrysts are common.

The porphyritic granite makes up the bulk of the intrusion and characteristically weathers into large bouldery wastes. The fine-grained type is only found along the eastern edge of the intrusion and is closely jointed, breaking into relatively small angular blocks upon weathering. In portion 46, Parish of Arthur's Seat, the Carboniferous rocks adjacent to the contact appear to be granitized. There was insufficient time on the present survey to study the internal structures of the granite mass, so that it is not possible to state whether the two types of granite represent two separate intrusions or whether the fine-grained type is a marginal phase of the porphyritic granite.

The age of the granite has never been definitely determined. It certainly intrudes the Lower Carboniferous (?) rocks and can definitely be regarded as post-Lower Carboniferous (?) as shown on Figure 1. The upper limit of the age is indefinite.

The main mass of the granite is situated to the west of and close to the coal measures and only isolated occurrences are found to the east. Outcrops are shown on the geological map of New South Wales east of Frazer's Creek, in the vicinity of Ashford and north-east of Bukkulla. A small outcrop near the village of Wandera is shown in Figure 1. A siliceous reef intrudes the Carboniferous near the eastern boundary of the coal measures and adjacent to the road, south of the coal mine. At most points along the western boundary of the coal measures there is a strip of Carboniferous rocks separating the measures from the granite. In the few places where there are no intervening rocks visible, the boundaries are obscured by waste. However, at no point was the granite seen to have actually intruded the coal measures. There is, therefore, no direct evidence that the granite was not pre-coal measures in age.* If it were as old as this it would probably have been intruded at the time of the Drummond orogeny. Under such circumstances any alteration of the coal would have been the result of compression during earth movements which gave rise to the faulting along the western edge of the present coal outcrop. On the other hand, the low volatile matter content of the coal may have been due to devolatilization caused by the granites being intruded subsequently to the coal measures being

* The writer has been informed that Professor David identified pebbles of granite in the Permian conglomerate (verbal communication from Dr. W. R. Browne). The possibility that these pebbles might have been derived from the adjacent granite strengthens the contention that it is pre-Permian in age.

laid down. The main mass of the porphyritic granite closely resembles the tin granites of New England, and these have been classified as Early Mesozoic by Andrews (1905) and as Late Permian by Browne (1929). The possibility of there being two separate intrusions of different age cannot be entirely overlooked.

The absence of definite evidence of the coal measures being intruded by the granite favours placing the age of the intrusion as pre-coal measures. However, the question has been left open for the present and the granite has been classified as post-Lower Carboniferous (?). Whatever the exact age, the intrusion shows a definite relationship to the structure of the country and the axis of injection of the granite and the direction of the strike of the fault forming the western boundary of the coal measures are closely related.

Basalts.

A large proportion of the southern half of the area is covered by Tertiary basalt flows. Easterly from Waterford's Creek the only outcrops of older rocks are along the MacIntyre River, Frying Pan Creek near Dinton Vale, and Vivers Gully near Wandera. On the other hand no outcrops of basalt were seen in the portion of the area north of the Parish of Arthur's Seat.

The basalts are typical of other Tertiary basalts found in New South Wales which have been described by Card (1903) and Browne (1933).

The basalts have been laterized in places. Some of these deposits have been described in connection with the survey of the bauxite resources of the State (Booker and Hanlon, 1944. Hanlon, 1944). Others occur near Oakwood and Dinton Vale. The Victorian aluminous laterites are either Lower Miocene or Lower Middle Miocene. It would take a considerable period for the formation of a laterite, so that if it is assumed that the laterization in New South Wales and Victoria was contemporaneous, it would make the basalts probably Oligocene or older in age.

The basalt flows probably modified the course of the MacIntyre River somewhat, but the valley is considered to occupy much the same position as in pre-basalt time. This question and the age of the basalt have been previously discussed more fully by the writer (Hanlon, 1944).

SUMMARY.

The coal measures at Ashford consist of a discontinuous belt over a distance of about 50 miles and have been laid down unconformably on Carboniferous (?) rocks. Except at one locality the dips in the coal measures are in a general westerly direction and the measures are apparently bounded on the west by a fault, probably in the nature of an overthrust. The Carboniferous (?) rocks have been intruded by granite. The granite may post-date the coal measures, although no evidence was seen that it intruded them. Oligocene (?) basalt flows have covered most of the southern portion of the area. Tertiary to Recent waste sheets, which are mostly thin, obscure most of the formation boundaries.

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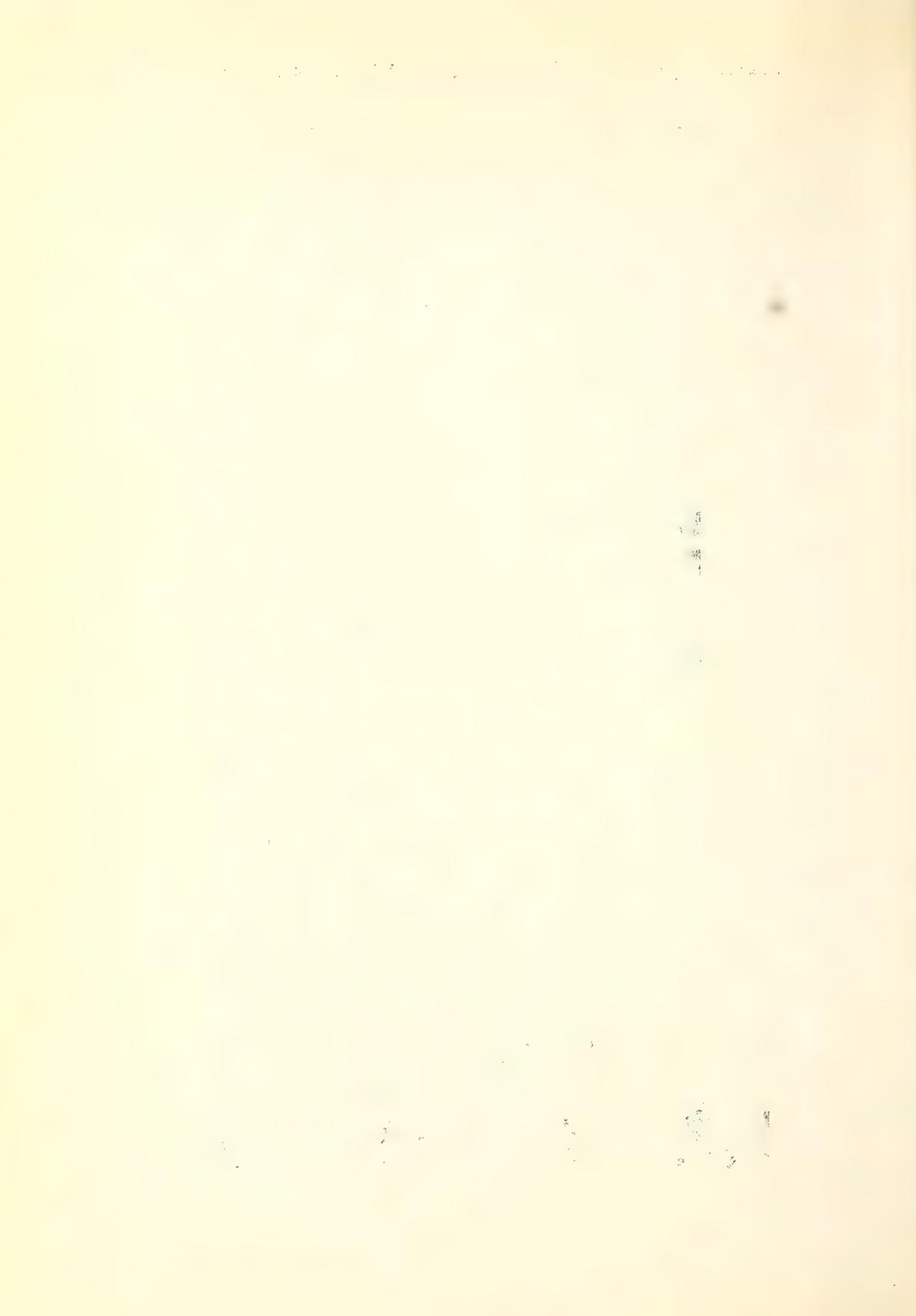
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EXPLANATION OF PLATE.

Fig. 1.—Northern face of Coal Gully, showing the almost right-angled unconformity between the Carboniferous (?), on the right of the photograph, and the Permian sediments. The junction is marked by a geological hammer.

Fig. 2.—Eastern bank of creek 70 chains to the south of Coal Gully. The geological hammer is on the unconformity between the Carboniferous (?), on the left of the photograph, and the Permian sediments.

OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1946.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

Manuscript received, February 3, 1947. Read, April 2, 1947.

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times either for personal effect or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the Nautical Almanac for 1938 and the reduction completed by the method given there. The necessary data were taken from the Nautical Almanac for 1946, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

Table I gives the observational material. The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table II gives the results of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the New Zodiacal Catalogue (Robertson, 1940) as recorded in the Nautical Almanac.

TABLE I.

Serial No.	N.Z.C. No.	Mag.	Date.	U.T.	Observer.
				h m s	
121	202	7.0	Mar. 6	9 13 31.2	R
122	469	7.3	Mar. 8	10 12 40.6	R
123	614	5.7	Mar. 9	8 56 55.4	W
124	1099	6.0	Mar. 12	10 44 27.6	W
125	1097	6.7	Mar. 12	10 49 34.2	W
126	1055	5.8	Apr. 8	8 26 23.3	R
127	1334	7.0	Apr. 10	10 22 53.3	R
128	1533	7.2	May 9	9 16 30.5	W
129	2097	7.1	July 8	13 08 23.2	W
130	1739	6.5	Aug. 1	9 23 49.6	W
131	1950	5.8	Aug. 3	9 24 30.8	W
132	2056	7.4	Aug. 4	9 39 32.3	W
133	2020	6.6	Aug. 31	10 24 55.8	W
134	2232	7.2	Sept. 2	9 58 36.8	R
135	2719	5.8	Oct. 3	9 42 45.8	W
136	3284	7.1	Oct. 7	13 56 27.2	W
137	2834	5.0	Oct. 31	12 39 38.4	W
138	2835	7.1	Oct. 31	12 50 55.0	W
139	3092	6.2	Nov. 2	12 38 50.6	W
140	3392	7.1	Dec. 29	11 56 19.4	W

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TABLE II.

Serial No.	Lunation.	p	q	p ²	pq	q ²	$\Delta\sigma$	p $\Delta\sigma$	q $\Delta\sigma$	Coefficient of	
										$\Delta\alpha$	$\Delta\delta$
121	287	97	+25	94	+24	6	"	"	"	+11.8	+0.62
122	287	78	-63	60	-49	40	+0.6	+0.5	0.0	+13.7	-0.33
123	287	34	-94	12	-32	88	+1.6	+0.5	-0.4	8.2	-0.81
124	287	+100	-7	100	-7	0	-0.4	-0.4	0.0	+13.5	-0.11
125	287	69	-72	48	-50	52	+1.1	+0.8	-0.8	9.0	-0.75
126	288	97	+25	94	+24	6	-1.1	-1.1	-0.3	+13.1	+0.25
127	288	+100	-2	100	-2	0	-0.6	-0.6	0.0	+13.5	-0.23
128	289	80	+60	64	+48	36	-2.6	-2.1	-1.6	+13.7	+0.29
129	291	78	-62	61	-49	39	+0.4	+0.3	-0.2	7.3	-0.87
130	292	76	+65	58	+49	42	-2.5	-1.9	-1.6	+14.3	-0.27
131	292	40	-92	16	-37	84	+2.6	+1.0	-2.4	0.1	-1.00
132	292	48	-88	23	-42	77	+2.6	+1.2	-2.3	+1.6	-1.00
133	293	98	-22	95	-22	5	-1.4	-1.4	+0.3	+12.0	-0.59
134	293	66	-75	44	-50	56	+0.2	+0.1	-0.2	+5.6	-0.92
135	294	97	+25	94	+24	6	+0.2	+0.2	0.0	+13.2	+0.21
136	294	94	-34	88	-32	12	-3.4	-3.2	-1.2	+14.3	0.00
137	295	88	+47	78	+41	22	-0.9	-0.8	-0.4	+11.5	+0.53
138	295	62	+78	39	+49	61	0.0	-0.4	-0.5	+7.6	+0.83
139	295	99	+11	99	+11	1	0.0	0.0	0.0	+13.1	+0.35
140	297	59	+81	35	+48	65	-0.6	-0.4	-0.5	+3.2	+0.98

NOTE ON p-p'-DINITRO DIPHENYL DISULPHIDE.

By G. K. HUGHES
and E. P. O'LEARY.

Manuscript received, February 3, 1947. Read, April 2, 1947.

In consequence of a recent paper on the above subject to Price and Stacy (1946),* it was thought opportune to record the following observations which confirm their findings that the so-called second form of dinitro diphenyl disulphide is a mixture of disulphide, monosulphide and sulphur.

The crude disulphide (prepared by the standard methods) was treated with a solution of sodium sulphide, which converted any disulphide into the soluble sodium salt of p-nitro thiophenol. The residue was given a second treatment with sodium sulphide and then recrystallised from acetone as golden flakes melting at 158-9° C., indicating that it was p-nitro phenyl monosulphide.

This was confirmed by oxidation to the sulphoxide and sulphone and comparing the three products with those of authentic p-nitro phenyl sulphide, sulphoxide and sulphone. The latter compound was reported by Fromm and Wittman (1908) to melt at 282° C. and by Bennett and Youle (1938) at 251° C.; our product also melted at 251° C.

The presence of free sulphur in the crude disulphide was indicated by extraction with hot acetone, cooling and recrystallising the precipitated solid from acetone. Analysis gave a sulphur content of approximately 28%, which is much higher than that required by the disulphide.

It was, of course, the importance of p-nitro benzene sulphonyl chloride that directed attention to the above and a series of experiments on the chlorine oxidation of the disulphide in aqueous acetic acid was carried out in order to find the best conditions. It is recommended that less than 5% of water is the most convenient, although up to 20% of water does not alter the yield of product.

It was part of our original programme to attempt the preparation of the oxidation products of the disulphide, but one of us (E.P.O'L.) was unable to continue.

Two attempts by standard methods to prepare the -SO₂-S- compound were unsuccessful.

EXPERIMENTAL.

The crude disulphide was prepared by the method of Bell (1928).

Isolation of p-Nitro phenyl sulphide.

The crude disulphide (1 part) was refluxed with acetone (3 parts) and filtered hot, and from the cooled red solution a yellow solid m.p. 137-8° C. collected. To a boiling suspension of this substance (5 g.) in water (75 ml.) was added a solution of sodium sulphide (5 g.) in water (20 ml.). The insoluble residue was treated in a similar way with sodium sulphide (1 g.) in water (10 ml.), washed with water and alcohol and recrystallised from acetone as golden flakes m.p. 158-9° C., mixed m.p. with p-nitro phenyl sulphide (Nietzki and Bothot (1894)) 158-9° C.

* For a complete bibliography, see the paper by Price and Stacy.

p-Nitro phenyl sulphoxide.

This was prepared from the crude disulphide, the sulphide as isolated above and the authentic sulphide, as follows :

Chlorine was passed into a suspension of the substance (2 g.) in glacial acetic acid (10 ml.) for about ninety minutes ; water added and the white precipitate collected, washed well with water ; repeated recrystallisation from glacial acetic acid gave white needles, m.p. 178-9° C.

Found : N, 9.6 ; S, 11.0%.

Calculated for $C_{12}H_8N_2O_3S$: N, 9.6 ; S, 11.0%.

p-Nitro phenyl sulphone.

This was prepared from both the monosulphide and sulphoxide. The sulphide (1 g.) was dissolved in hot glacial acetic acid (10 ml.) and a solution of chromic acid (potassium dichromate (1.5 g.), water (20 ml.) and sulphuric acid (14 ml.)) was added gradually with stirring. After dilution with water, the solid was collected and recrystallised from glacial acetic acid as white feathery needles, m.p. 250-1° C. The yield in both cases was almost quantitative.

Chlorine Oxidation of Crude Disulphide.

This was carried out following the method of Loudon and Shulman (1938) with various percentages of water.

The sulphonyl chloride was estimated by titrating with alcoholic silver nitrate and ammonium thiocyanate.

Five grammes of crude disulphide were used in each experiment.

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A NEW METHOD OF APPROXIMATING THE BINOMIAL AND HYPERGEOMETRIC PROBABILITIES.

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I. THE BINOMIAL CASE.

Let P_r denote the probability of exactly r successes in n trials if at each trial the probability of a success is p . Instead of using Stirling's formula and expanding $\log_e P_r$ in powers of n^{-1} , as originated by De Moivre and Laplace (Todhunter, §§333, 993), the idea is to expand $\log_e \frac{P_{r+1}}{P_r}$, which is $\Delta \log_e P_r$;

then to derive $\frac{d}{dr} \log_e P_r$ by means of such formulas as (Boole, pp. 25, 89)

$$f'(x) = \Delta f(x) - \frac{1}{2} \Delta^2 f(x) + \frac{1}{3} \Delta^3 f(x) - \dots \dots \dots (1)$$

$$f'(x) = \left(1 - \frac{1}{2} \frac{d}{dx} + \frac{1}{12} \frac{d^2}{dx^2} - \dots \right) \Delta f(x) \dots \dots \dots (2)$$

the interval being 1; and to solve the simple differential equation.

This is less direct than the classical procedure, but the algebra is less cumbrous, the construction of the expansion is clearer, and choice of terms for various orders of approximation is made more easily.

We shall take $p \leq q$, as the same analysis is applicable in the complementary case of the number of failures $s (= n - r)$ if $q < p$. We have $P_{r+1}/P_r = \frac{n-r}{r+1} \cdot \frac{p}{q}$,

where $q = 1 - p$, or, putting $r = np + x$, and writing P_x for P_r to indicate the substitution, $P_{x+1}/P_x = \frac{p(nq-x)}{q(np+x+1)} = \frac{1-px/v}{1+q(x+1)/v}$, where $v = npq \dots \dots (3)$

Expanded in powers of (v^{-1}) ,

$$\begin{aligned} \log P_{x+1} - \log P_x = & -\frac{px}{v} - \frac{p^2x^2}{2v^2} - \frac{p^3x^3}{3v^3} - \dots \\ & - \frac{q(x+1)}{v} + \frac{q^2(x+1)^2}{2v^2} - \frac{q^3(x+1)^3}{3v^3} + \dots \dots \dots (4) \end{aligned}$$

$$\begin{aligned} \text{or } \Delta \log P_x = & -\frac{(q+p)x+q}{v} + \frac{(q^2-p^2)x^2+q^2(2x+1)}{2v^2} \\ & - \frac{(q^3+p^3)x^3+q^3(3x^2+3x+1)}{3v^3} + \dots \dots \dots (5) \end{aligned}$$

When r is near np , i.e. when x is $O(1)$, both terms (distinguished according to powers of x) of the first group are $O(v^{-1})$, the three terms of the second group are $O(v^{-2})$, and so on. When $|x|$ increases to $O(v^{\frac{1}{2}})$, the terms of the successive groups are $O(v^{-\frac{3}{2}}, v^{-1})$, $O(v^{-1}, v^{-\frac{3}{2}}, v^{-2})$, and so on.

For values of x ranging from $O(1)$ to $O(v^{\frac{1}{2}})$ we may then evaluate $\Delta \log P_x$ with various degrees of approximation, by neglecting terms of (5) which are of higher than a specified order of smallness *throughout* this range of x .

First Approximation to P_r .

Neglecting terms of order higher than $O(v^{-\frac{1}{2}})$, we have

$$\Delta \log P_x = -\frac{(q+p)x}{v} = -\frac{x}{v} \dots\dots\dots (6)$$

$$\Delta^2 \log P_x = -\frac{1}{v} = 0 \text{ to } O(v^{-\frac{1}{2}}), \text{ and } \Delta^3 \log P_x = 0.$$

Hence by (1), $\frac{d}{dx} \log P_x = -\frac{x}{v}$ to $O(v^{-\frac{1}{2}})$ (7)

and $P_x = h \exp\left(-\frac{x^2}{2npq}\right)$, h being a constant of integration (8)

Second Approximation to P_r .

Neglecting terms of order above $O(v^{-1})$, we have

$$\Delta \log P_x = -\frac{x+q}{v} + \frac{(q-p)x^2}{2v^2} \dots\dots\dots (9)$$

$$\Delta^2 \log P_x = -\frac{1}{v}, \text{ as } \frac{(q-p)(2x+1)}{2v^2} \text{ is } O(v^{-\frac{3}{2}}) \text{ at lowest,}$$

$$\Delta^3 \log P_x = 0.$$

Hence by (1), $\frac{d}{dx} \log P_x = -\frac{x+q}{v} + \frac{1}{2v} + \frac{(q-p)x^2}{2v^2}$
 $= -\frac{x}{v} - \frac{q-p}{2v} \left(1 - \frac{x^2}{v}\right)$ to $O(v^{-1})$ (10)

and $P_x = k \exp\left[-\frac{x^2}{2v} - \frac{q-p}{2v} \left(x - \frac{x^3}{3v}\right)\right]$, k being a constant; or,

writing $t = \frac{x}{\sqrt{v}} = \frac{r-np}{\sqrt{npq}}$, which is $O(1)$ when x is $O(v^{\frac{1}{2}})$,

$$P_t = k \exp\left[-\frac{1}{2}t^2 - \frac{q-p}{2\sqrt{v}} \left(t - \frac{1}{3}t^3\right)\right] \dots\dots\dots (11)$$

$$= ke^{-\frac{1}{2}t^2} \left\{1 - \frac{q-p}{2\sqrt{v}} \left(t - \frac{1}{3}t^3\right)\right\} \dots\dots\dots (12)$$

In deriving (12) from (11) we neglect terms $O(v^{-1})$ in the expansion of $\exp\left[-\frac{q-p}{2\sqrt{v}} \left(t - \frac{1}{3}t^3\right)\right]$, for to retain them would be equivalent to retaining terms $O(v^{-\frac{3}{2}})$ in (10). As may be anticipated, it will presently appear that k is $O(v^{-\frac{1}{2}})$, and therefore that (12) is an approximation to $O(v^{-1})$ as intended.

To determine the constant k , we have, assuming that (12) is effective throughout the range of x ,

$$1 = \sum_{r=0}^n P_r = \sum_{x=-np}^{nq} P_x = \sum_{t=-np/\sqrt{v}}^{nq/\sqrt{v}} P_t, \text{ the interval for } t \text{ being } 1/\sqrt{v}. \text{ Hence}$$

by an Euler-Maclaurin formula (Milne-Thomson, p. 190),

$$1 = \sqrt{v} \int_{-(np+\frac{1}{2})/\sqrt{v}}^{(nq+\frac{1}{2})/\sqrt{v}} \frac{P_t dt}{24\sqrt{v}} \left\{ \frac{P'}{(nq+\frac{1}{2})/\sqrt{v}} - \frac{P'}{-(np+\frac{1}{2})/\sqrt{v}} \right\} + \dots \dots \dots (13)$$

In such a case as $n=20, p=0.3, q=0.7$, we have $np=6, nq=14, v=npq=4.2, \sqrt{v}=2.05$, and from (12) the integral in (13) is

$$k\sqrt{(2\pi v)} \left[\frac{1}{\sqrt{2\pi}} \int e^{-\frac{1}{2}t^2} dt + \frac{(q-p)(1-t^2)}{6\sqrt{v}} \cdot \frac{e^{-\frac{1}{2}t^2}}{\sqrt{2\pi}} \right]_{-3.17}^{7.1} \dots \dots \dots (14)$$

From K. Pearson's tables of areas and ordinates of the normal frequency curve, it appears that the value of the first term in the square bracket is 0.9992, of the second, 0.0008, and of the second term in (13), less than 0.0001. So in this case k is sensibly $\frac{1}{\sqrt{(2\pi v)}}$. Likewise if $n=100, p=0.1$, then $np=10, v=npq=9, \sqrt{v}=3$, and the apparent error of taking $\frac{1}{\sqrt{(2\pi v)}}$ for the constant is of similar magnitude.

So for quite moderate values of npq such as often occur in practice, we are led to the well-known formula (Uspensky, p. 135, Ex. 7),

$$P_r = \frac{1}{\sqrt{(2\pi npq)}} e^{-\frac{1}{2}t^2} \left\{ 1 - \frac{(q-p)(3t-t^3)}{6\sqrt{(npq)}} \right\} \text{ where } t = \frac{r-np}{\sqrt{(npq)}} \dots \dots \dots (15)$$

The practising statistician is most interested in areas of tails in order to estimate "significance levels." The probability that $r \leq r_1$ is $\sum_{r=0}^{r_1} P_r$ and $\sum_{r=0}^{r_1} P_r = \frac{1}{\sqrt{2\pi}} \left[\int e^{-\frac{1}{2}t^2} dt + \frac{(q-p)(1-t^2)}{6\sqrt{(npq)}} e^{-\frac{1}{2}t^2} \right]_{-\infty}^{t_1}$, where $t_1 = (r_1 + \frac{1}{2} - np) / \sqrt{(npq)}$, and for $r \geq r_2$ the limits are $(r_2 - \frac{1}{2} - np) / \sqrt{(npq)}$ and ∞ $\dots \dots \dots (16)$

When r_1 and r_2 are equidistant from np or nearly so, and $r_1 < np < r_2$, the sum of these probabilities is $1 - \frac{2}{\sqrt{2\pi}} \int_0^{t_m} e^{-\frac{1}{2}t^2} dt$ nearly, where t_m is the mean of the absolute values of the finite limits. This is equivalent to Laplace's form (Uspensky, p. 130), and in practice is regarded as giving the significance level usually with sufficient accuracy, provided that we define "significance level" in the case of discrete distributions as the sum of the probabilities of values which are about as probable as, or less probable than, the observed value, and find by means of (15) the best companion value r_2 to go with an observed r_1 , and *vice versa*.

Accuracy of the Approximate Evaluation.

If, as in (14), the lower limit $-(np + \frac{1}{2})/\sqrt{v} \gg \sqrt{10}$, there is no difficulty in confirming $1/\sqrt{(2\pi v)}$ within a few units per 1,000 as the constant appropriate to the second approximation. Supposing this limitation accepted, we

$$\text{should have } \frac{n^2 p^2 + np + \frac{1}{4}}{np} \gg 10(1-p), \text{ or } p \gg \frac{9}{n+10} \text{ nearly } \dots\dots\dots (17)$$

But, of course, fulfilment of this, or a more, or less, stringent condition, would not imply a corresponding degree of accuracy in the approximate formula. For example, if $n=8, p=\frac{1}{2}$, it may be verified as in (14) that the derived constant differs from $1/\sqrt{(2\pi v)}$ by less than 2 per 1,000, but the errors committed by using the approximate formula range from 0.001 to 0.008 in absolute value.

Professor J. V. Uspensky, in his Chap. 7, emphasizes the importance of knowing how large an error may be committed and gives several upper limits. For the error E in P_r as computed from (15) herein, he finds (Uspensky, p. 135)

$$|E| < \frac{0.15 + 0.25 |q-p|}{(npq)^{\frac{3}{2}}} + e^{-\frac{3}{2}\sqrt{(npq)}}, \text{ provided } npq \gg 25 \dots (18)$$

As the proviso indicates, this formula is not suitable for cases in which npq is comparatively small. In the case above mentioned where $n=8, p=\frac{1}{2}, npq=2$, it gives $|E| < 0.17$, which is about 20 times the actual maximum error committed. It is possible, however, to deduce from higher approximations to P_r closer limits than the above for the errors committed by using the classical second approximation.

Denoting by $P_r^{(s)}$ the value of P_r obtained by the s th approximation, we may first note that by (8) and (15)

$$E_1 \equiv P_r^{(1)} - P_r^{(2)} = \frac{1}{\sqrt{(2\pi npq)}} e^{-\frac{1}{2}t^2} \frac{(q-p)(3t-t^3)}{6\sqrt{(npq)}} \text{ where } t = \frac{r-np}{\sqrt{(npq)}} \dots (19)$$

Differentiating with regard to t , we find critical points for E_1 at $t^2 = 3 \pm \sqrt{6}$ and, using the tables, that the lower sign gives the numerical maximum.

$$\text{Hence } |E_1| < \frac{0.1 |q-p|}{npq} \dots\dots\dots (20)$$

Third Approximation to P_r .

Some little advantage is gained in the higher approximations if we sidetrack the calculation of $\Delta^2, \Delta^3, \dots$ by using (2) instead of (1).

Applying (2) to (4) we have

$$\frac{d}{dx} \log P_x = \sum_{s=1}^{\infty} \left\{ -\frac{p^s B_s(x)}{v^s s} + \frac{q^s B_s(x+1)}{(-v)^s s} \right\}$$

$$\text{Hence } \log P_x = C + \sum_{s=1}^{\infty} \left\{ -\frac{p^s B_{s+1}(x)}{v^s s(s+1)} + \frac{q^s B_{s+1}(x+1)}{(-v)^s s(s+1)} \right\}, \dots\dots\dots (21)$$

where the constant elements of Bernoulli's polynomials $B_s(x)$, etc., are now absorbed in C . (In virtue of the property $\Delta B_r(x) = rx^{r-1}$, (21) may be written direct from the difference equation (4).) Noting that $B_r(x+1) =$

$B_r(x) + rx^{r-1}$ (Milne-Thomson, pp. 136-141) we have

$$P_x = K \exp \left\{ \frac{-p(x^2-x) - q(x^2+x)}{2v} + \frac{-p^2 \left(x^3 - \frac{3}{2}x^2 + \frac{1}{2}x \right) + q^2 \left(x^3 + \frac{3}{2}x^2 + \frac{1}{2}x \right)}{6v^2} \right. \\ \left. + \frac{-p^3(x^4 - 2x^3 + x^2) - q^3(x^4 + 2x^3 + x^2)}{12v^3} \right. \\ \left. + \frac{-p^4 \left(x^5 - \frac{5}{2}x^4 + \frac{5}{3}x^3 - \frac{1}{6}x \right) + q^4 \left(x^5 + \frac{5}{2}x^4 + \frac{5}{3}x^3 - \frac{1}{6}x \right)}{20v^4} \right. \\ \left. + \frac{-p^5 \left(x^6 - 3x^5 + \frac{5}{2}x^4 - \frac{1}{2}x^2 \right) - q^5 \left(x^6 + 3x^5 + \frac{5}{2}x^4 - \frac{1}{2}x^2 \right)}{30v^5} + \dots \right\}$$

and putting $t = xv^{-\frac{1}{2}} = \frac{r-np}{\sqrt{npq}}$,

$$P_r = K \exp \left\{ \frac{-(q+p)t^2}{2} + \frac{-3(q-p)t + (q^2-p^2)t^3}{6v^{\frac{1}{2}}} + \frac{3(q^2+p^2)t^2 - (q^3+p^3)t^4}{12v} \right. \\ \left. + \frac{5(q^2-p^2)t - 10(q^3-p^3)t^3 + 3(q^4-p^4)t^5}{60v^{\frac{3}{2}}} \right. \\ \left. + \frac{-10(q^3+p^3)t^2 + 15(q^4+p^4)t^4 - 4(q^5+p^5)t^6}{120v^2} \right. \\ \left. + \dots \right\} \dots \dots \dots (22)$$

The first two terms are those required for the second approximation already dealt with. The next is additional for the third approximation, the following for the fourth, and so on. The alternation in sign of $(q^h \mp p^h)$ according to odd and even powers of t and $v^{\frac{1}{2}}$ is noteworthy.

Putting $g = q - p$, we have $q^h \pm p^h = \frac{1}{2^h} \{ (1+g)^h \pm (1-g)^h \} \dots \dots \dots (23)$

and for the third approximation

$$P_r^{(3)} = K \exp \left\{ -\frac{1}{2}t^2 - \frac{g(3t-t^3)}{6v^{\frac{1}{2}}} + \frac{6(1+g^2)t^2 - (1+3g^2)t^4}{48v} \right\} \\ = Ke^{-\frac{1}{2}t^2} \left\{ 1 - \frac{g(3t-t^3)}{6v^{\frac{1}{2}}} + \frac{\frac{2}{3}g^2(3t-t^3)^2 + 6(1+g^2)t^2 - (1+3g^2)t^4}{48v} \right\} \\ \dots \dots \dots (24)$$

to $O(v^{-1})$ in $\{ \}$, i.e. to $O(v^{-\frac{3}{2}})$ in $P_r^{(3)}$.

Determining the constant as in (13), (14), we have

$$\frac{1}{K} = \sqrt{(2\pi v)} \left\{ 1 + \frac{\frac{2}{3}g^2(9-18+15) + 6(1+g^2) - 3(1+3g^2)}{48v} \right\} \\ \text{or } K = 1 / \left\{ \left(1 + \frac{3-g^2}{48v} \right) \sqrt{(2\pi v)} \right\} \dots \dots \dots (25)$$

Recalling that $P_r^{(2)} = \frac{1}{\sqrt{(2\pi v)}} e^{-\frac{1}{2}t^2} \left\{ 1 - \frac{g(3t-t^3)}{6v^{\frac{1}{2}}} \right\}$, we have to $O(v^{-\frac{3}{2}})$

$$E_2 = P_r^{(2)} - P_r^{(3)} = \frac{1}{\sqrt{(2\pi v)}} e^{-\frac{1}{2}t^2} \cdot \frac{1}{48v} \{ 3 + g^2 - \frac{2}{3}g^2(3t-t^3)^2 - 6(1+g^2)t^2 + (1+3g^2)t^4 \} \dots\dots\dots(26)$$

or $E_2 = \frac{e^{-\frac{1}{2}t^2} F}{48v^{\frac{3}{2}} \sqrt{2\pi}}$, where $F = (3 - 6t^2 + t^4) + g^2(1 - 12t^2 + 7t^4 - \frac{2}{3}t^6)$
 $= A + g^2 B.$

Differentiating, we find that A has critical values at $t=0, t^2=3$, and B at $t=0, t^2=1, 6$. The course of E_2 may be examined in the following schedule, which shows that only when g^2 is nearly 1 is there a value of t^2 , viz. 1 nearly, which vies with $t=0$ to produce the numerical maximum value of E_2 .

Hence $|E_2| < \frac{0.399(3+g^2)}{48v^{\frac{3}{2}}} \times \frac{1.624}{1.596} < \frac{0.0254\{1 + \frac{1}{3}(g-p)^2\}}{(npq)^{\frac{3}{2}}}$, (27)

where the decimal may be read as 0.025 for all cases in which $p > 0.01$.

Schedule of Elements of Value of E_2 .

t^2	t	$\frac{e^{-\frac{1}{2}t^2}}{\sqrt{2\pi}}$	A	B	$\frac{(A+B)e^{-\frac{1}{2}t^2}}{\sqrt{2\pi}}$
0	0	0.399	3	1	1.596
.25	.5	.352	1.56	-1.57	
.55	.742	.304	0	-3.59	
.90	.949	.254	-5.94	-4.62	-1.576
.95	.975	.248	-1.80	-4.65	-1.600
1.0	1.0	.242	-2.0	-4.67	-1.613
1.05	1.025	.236	-2.20	-4.65	-1.617
1.1	1.049	.230	-2.39	-4.62	-1.612
2.0	1.414	.147	-5.0	-0.33	
3.0	1.732	.089	-6.0	10.0	
3.5	1.872	.070	-5.8	16.2	
4.0	2.0	.054	-5.0	22.3	
5.0	2.235	.033	-2.0	32.7	
6.0	2.450	.020	3.0	37.0	
7.0	2.636	.013	10.0	35.8	

Further Approximations to P_r .

Applying (23), we may write (22) as

$$P_r = K \exp \{ -\frac{1}{2}t^2 + av^{-\frac{1}{2}} + bv^{-1} + cv^{-\frac{3}{2}} + dv^{-2} + \dots \}$$

where $a = -\frac{1}{6}g(3t-t^3)$,

$$b = \frac{1}{48} \{ 6(1+g^2)t^2 - (1+3g^2)t^4 \}$$

$$c = \frac{1}{120} g \{ 10t - 5(3+g^2)t^3 + 3(1+g^2)t^5 \}$$

$$d = \frac{1}{960} \{ -20(1+3g^2)t^2 + 15(1+6g^2+g^4)t^4 - 2(1+10g^2+5g^4)t^6 \} \dots\dots\dots(28)$$

Expanding $\exp(av^{-\frac{1}{2}} + bv^{-1} + cv^{-\frac{3}{2}} + dv^{-2} + \dots)$, we have

$$P_r = Ke^{-\frac{1}{2}t^2} \left\{ 1 + av^{-\frac{1}{2}} + \left(\frac{1}{2}a^2 + b\right)v^{-1} + \left(ab + \frac{1}{6}a^3 + c\right)v^{-\frac{3}{2}} + \left(ac + \frac{1}{2}a^2b + \frac{1}{24}a^4 + \frac{1}{2}b^2 + d\right)v^{-2} + \dots \right\} \dots \dots (29)$$

As the terms with odd powers of $v^{-\frac{1}{2}}$ involve only odd powers of t , the constant for $P^{(2)}$ is the same as for $P^{(1)}$, as already noted, and now the constant for $P^{(4)}$ is the same as for $P^{(3)}$, viz. from (25), $1/(1 + hv^{-1})\sqrt{(2\pi v)}$, where $h = \frac{3 + g^2}{48}$.

We further calculate the constant for $P^{(5)}$ as $1/(1 + hv^{-1} + \frac{1}{2}h^2v^{-2})\sqrt{(2\pi v)}$, which, to the order calculated, is $e^{-hv^{-1}}(2\pi v)^{-\frac{1}{2}}$ (30)

Hence, writing Y for $e^{-\frac{1}{2}t^2}(2\pi v)^{-\frac{1}{2}}$, we have successively,

$$\begin{aligned} P^{(1)} - P^{(2)} &= -Yav^{-\frac{1}{2}} \text{ to } O(v^{-1}) \\ P^{(2)} - P^{(3)} &= -Y\left(\frac{1}{2}a^2 + b - h\right)v^{-1} \text{ to } O(v^{-\frac{3}{2}}) \text{ which have been calculated above;} \\ P^{(3)} - P^{(4)} &= -Y\left(ab + \frac{1}{6}a^3 + c - ha\right)v^{-\frac{3}{2}} \text{ to } O(v^{-2}), \text{ and} \\ P^{(4)} - P^{(5)} &= -Y\left(ac + \frac{1}{2}a^2b + \frac{1}{24}a^4 + \frac{1}{2}b^2 + d - h\left(\frac{1}{2}a^2 + b\right) + \frac{1}{2}h^2\right)v^{-2} \text{ to } O(v^{-\frac{5}{2}}) \end{aligned}$$

. (31)

Examining $E_3 \equiv P^{(3)} - P^{(4)}$ as above, we find $|E_3| < \frac{0 \cdot 02 |q - p|}{(npq)^2}$

. (32)

Summary of Limits.

It is not an object of this paper to find upper limits of error in order to prove Bernoulli's theorem rigidly. This has been done by Professor Uspensky. The idea is merely to find close and convenient limits for use by the practising

statistician. Three limits are available: $|E_1| \equiv |P_r^{(1)} - P_r^{(2)}| < \frac{0 \cdot 1 |q - p|}{npq}$,
 $|E_2| \equiv |P_r^{(2)} - P_r^{(3)}| < \frac{0 \cdot 0254 \{1 + \frac{1}{3}(q - p)^2\}}{(npq)^{\frac{3}{2}}}$, $|E_3| \equiv |P_r^{(3)} - P_r^{(4)}| < \frac{0 \cdot 02 |q - p|}{(npq)^2}$.

E_4 might, doubtless, be expressed as a function of $(q - p)$, but it may suffice to find its maximum when $q = 1$ (the Poisson case, which gives the largest errors), which occurs when $t^2 = 1 \cdot 66$. Hence $|E_4| \equiv |P_r^{(4)} - P_r^{(5)}| < \frac{0 \cdot 016}{(npq)^{\frac{5}{2}}}$.

Because the numerically greatest values of E_1, E_2, E_3 occur at different values of t , e.g. when $q = 1$, at $t^2 = 0 \cdot 55, (0 \text{ and } 1 \cdot 05), 1 \cdot 38$ respectively, the limits are not additive, and so $|P_r^{(1)} - P_r^{(3)}| < |E_1| + |E_2|$ and so on. This might, of course, be remedied if thought necessary, by considering maximum values of $e^{-\frac{1}{2}t^2}F$, where F contains both odd and even powers of it, but the disjointed method by which F contains either odd or even powers presents a simpler task.

The error of the classical approximation is, perhaps, of the greatest interest. In all cases calculated by the writer, except those where p is very small, the formula for E_2 gives a true and close upper limit. For example, when (a) $n = 20, p = 0 \cdot 3, npq = 4 \cdot 2$; (b) $n = 100, p = 0 \cdot 1, npq = 9$; (c) $n = 8, p = 0 \cdot 5, npq = 2$; (d) $n = 100, p = 0 \cdot 5, npq = 25$; the maximum error of P_r is covered by the formula for $|E_2|$. In this last case the Uspensky formula gives nearly nine times the maximum. It is also noted by the way, that, in this case, the

third approximation to P_r ((24) with constant (25)), gives P_r with an error ≤ 0.00001 . On the other hand, for $n=1256$, $p=0.005$, $npq=6.25$, the formula gives $|E_2| < 0.0022$, whereas the actual maximum error is 0.0023 . This is easily covered by including $|E_3|$.

II. THE HYPERGEOMETRIC CASE.

This is the realistic statistical case of sampling from a finite population without replacement. From a population consisting of Np ayes and Nq noes a random sample of n is drawn. Denoting by P_r the probability that the sample

contains exactly r ayes, we have $P_r = \binom{Np}{r} \cdot \binom{Nq}{n-r} / \binom{N}{n}$

Hence $P_{r+1}/P_r = \frac{n-r}{r+1} \cdot \frac{Np-r}{Nq-n+r+1}$, which, when N is large in comparison

with n , approximates to the binomial form $\frac{(n-r)p}{(r+1)q}$ treated above. To include

cases when N and n are comparable, by putting $r=np+x$, $v=npq$, $w=(N-n)pq$,

we have $P_{r+1}/P_r = \frac{1-px/v}{1+q(x+1)/v} \cdot \frac{1-qx/w}{1+p(x+1)/w}$. Proceeding as in *I*, we find,

in parallel with the expression following (10), for the second approximation to P_r ,

$$P_r = k \exp \left[-\frac{x^2}{2npq} - \frac{q-p}{2npq} \left(x - \frac{x^3}{3npq} \right) - \frac{x^2}{2(N-n)pq} + \frac{q-p}{2(N-n)pq} \left\{ x - \frac{x^3}{3(N-n)pq} \right\} \right] \dots \dots \dots (33)$$

the lower line of the exponential being obtainable from the upper by substituting $(N-n)$ for n and interchanging p and q , and k being a constant to be determined. Hence

$$P_r = k \exp \left[-\frac{x^2}{2pqn \left(1 - \frac{n}{N} \right)} - \frac{(q-p)}{2pq} \left\{ \frac{x \left(1 - \frac{2n}{N} \right)}{n \left(1 - \frac{n}{N} \right)} - \frac{x^3 \left(1 - \frac{2n}{N} \right)}{3pqn^2 \left(1 - \frac{n}{N} \right)^2} \right\} \right] \dots \dots \dots (34)$$

Writing σ for $\sqrt{\left\{ npq \left(1 - \frac{n}{N} \right) \right\}}$ and t for $\frac{x}{\sigma}$, this becomes after expanding the second term of the exponential,

$$P_r = ke^{-\frac{1}{2}t^2} \left\{ 1 - \frac{(q-p) \left(1 - \frac{2n}{N} \right)}{2\sigma} \left(t - \frac{1}{3}t^3 \right) \right\} \dots \dots \dots (35)$$

which differs in form from the corresponding binomial expression (12) only through the factor $\left(1 - \frac{2n}{N} \right)$ in the correction term.

As for the constant k , the conditions for finding that this should be sensibly $\frac{1}{\sigma\sqrt{2\pi}}$ where $\sigma = \sqrt{\left\{ npq\left(1 - \frac{n}{N}\right)\right\}}$, are the more easily fulfilled as the present σ is less than $\sqrt{(npq)}$, its value in the binomial case. For example, to correspond

$$\text{with (17), viz. } p \gg \frac{9}{n+10} \text{ nearly, we now have } p \gg \frac{9-10n/N}{n+10-10n/N} \dots \quad (36)$$

which in the case of a 30% sample is $6/(n+7)$.

The cumulative probability corresponding to (16) for the binomial case is

$$\sum_{r=0}^{r_1} P_r = \frac{1}{\sqrt{2\pi}} \left[\int e^{-\frac{1}{2}t^2} + \frac{(q-p)\left(1 - \frac{2n}{N}\right)}{\sigma\sqrt{\left\{ npq\left(1 - \frac{n}{N}\right)\right\}}} (1-t^2)e^{-\frac{1}{2}t^2} \right]_{-\infty}^{t_1} \dots \dots \dots (37)$$

where $t_1 = (r_1 + \frac{1}{2} - np) / \sqrt{\left\{ npq\left(1 - \frac{n}{N}\right)\right\}}$.

The error limits for the hypergeometric P_r as well as for "significance levels" for both cases, and the reason why the modern French approximation (Borel, p. 45) is inferior to Laplace's may be the subjects of a further paper.

It may be noted that the expansion of the binomial P_r may be written

$$P = P^{(1)} + (P^{(2)} - P^{(1)}) + (P^{(3)} - P^{(2)}) + \dots$$

where $P^{(1)} = (2\pi v)^{-\frac{1}{2}} e^{-\frac{1}{2}t^2}$ and the bracketed terms have the values given by (31). It can be verified that this series agrees with H. Cramér's asymptotic expansion (Cramér, p. 87). For example, in the line following (26) we have

$$F = H_4(t) - g^2\{3H_4(t) + \frac{2}{3}H_6(t)\}$$

where $H_4(t)$ and $H_6(t)$ are the 4th and 6th Hermite polynomials. The 3rd and 4th semi-invariants of the binomial distribution being $K_3 = vg$ and $K_4 = -\frac{1}{2}v(1-3g^2)$, it follows that $(P^{(3)} - P^{(2)})$ agrees with Cramér's $P_{2n}(-\Phi)$, and so on.

On the other hand, the Type A series (Charlier, Bruns, Gram and Thiele) gives for this term $(1-3g^2)H_4(t)$, the portion involving $H_6(t)$ being deferred (Cramér, p. 88), and it is found that differentiation of the expression for $(P^{(3)} - P^{(2)})$ thus truncated does not closely locate that value of t which shows the greatest numerical error, as does equivalent treatment of the full expression. So it appears that in the case of the binomial asymptotic expansion, if $q \neq p$, the rearrangement of terms involved in the simpler Type A form (Rietz, p. 158) retards the convergency.

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CORRIGENDUM.

In the present writer's paper "Elementary Presentation of the Frequency Distributions . . ." (THIS JOURNAL, Vol. LXXIV, pp. 209-239), at p. 238, line 22, instead of the first variate read $\sqrt{n} \cdot (\bar{X} - A)/\sigma$, for, writing v_1 and v_2 for the variates in line 20, the appropriate orthogonal transformation is $\frac{v_1\sqrt{n_1} + v_2\sqrt{n_2}}{\sqrt{(n_1 + n_2)}}$, $\frac{v_1\sqrt{n_2} - v_2\sqrt{n_1}}{\sqrt{(n_1 + n_2)}}$, which gives the correct new pair of variates.

STUDIES IN SEMIQUINONES.

PART I. p-PHENYLENE DIAMINE AND BENZIDINE DERIVATIVES.

By G. K. HUGHES and N. S. HUSH.

Manuscript received, April 16, 1947. Read, May 7, 1947.

The most recent theory of the structure of Wurster type dyes (oxidation products of p-phenylene diamines) is that of Michaelis and Granick (1943).

The amines from which these authors prepared their crystalline δ -salts¹ include 1:4-diaminobenzene, 1:4(bis)-methylaminobenzene, 1-amino,4-dimethylaminobenzene, 1-dimethylamino,4-methylaminobenzene and 1:4(bis)-dimethylaminobenzene.

The anions, used to precipitate the organic cations as salts, were perchlorate, iodide and bromide.

The main conclusions of Michaelis and Granick are as follows:

(1) In dilute solution Wurster salts are free resonance-stabilized semiquinone ions; at low temperatures and high concentrations they may polymerize, in which case there is an equilibrium between the monomeric and the polymeric forms.

(2) The solid δ -salts are either wholly in the s-form or wholly in the π -form.

(3) Polymerization will occur only when the parent diamine has at least one unsubstituted hydrogen atom on one of its amino groups.

(4) If all the amino hydrogen atoms are substituted, no dimeric bond can be established, and the compound remains a free radical even in the solid state.

(5) The polymerized molecule is a linear resonating structure in which the moieties involved in the exchange are diamine and diiminium ion (with a double positive charge). The two rings lie in the same plane and the four atoms attached to the central N atoms lie in a plane perpendicular to that of the benzene rings. The steric hindrance of alkyl groups weakens the bond (formed by the exchange of an electron pair between the two central N atoms) and makes the compound unstable.

¹The nomenclature, used in this paper for the solid salts, is an extension of that of Michaelis, Granick and Schubert (1940), and Michaelis and Granick (1943). The salt is named by reference to the diamine from which it is derived and the anion used to precipitate the organic cation. Four prefixes are employed:

δ -Salts are those which are on the oxidation level of semiquinones. In using this prefix no commitment is made as to whether the salt is a free radical or a polymer. δ -Salts may be subdivided into two classes:

(a) s-Salts are salts of monomeric free semiquinone ions.

(b) π -Salts are those in which the semiquinone ions are polymerised. In agreement with the above-mentioned authors, no distinction is made between dimers and higher polymers; the dimeric unit is convenient for illustrating the theory and is always referred to, but this does not exclude the possibility of the resonance extending over the entire crystal.

ω -Salts are the almost colourless hygroscopic salts on zero oxidation level obtained from some s- and π -salts on standing.

This paper contains experimental evidence which conflicts with statements (2), (3) and (4) and shows that (5) must be modified; alternative explanations of the facts brought forward by Michaelis and Granick are advanced.

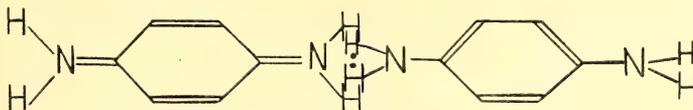


Fig. 1.—The axes of the two benzene rings are co-linear and the rings are co-planar. The central imino- and amino-H atoms lie at the vertices of a square perpendicular to the plane of the ring.

Before presenting these it may be pointed out that while the Michaelis-Granick theory of the dimeric resonance bond is consistent both with resonance theory and with experiment in the meriquinone field in so far as it postulates resonance between forms which possess a quinoid and a hydroquinoid part, the theory is inconsistent with experimental evidence adduced by these authors when it postulates that the moieties of each resonant state must have a linear coplanar arrangement.

This latter postulate requires that the atoms or groups attached to the central resonance-bonded nitrogen atoms are linked to a different nitrogen atom in each limiting state. While this is conceivable in the case of the δ -salts of 1:4-diaminobenzene, in which the atoms concerned are hydrogen, it cannot explain the formation of the dimeric bond in the δ -salts of 1:4-(bis)-methylaminobenzene, 1-amino:4-dimethylaminobenzene and 1-dimethylamino:4-methylaminobenzene, for this would require that in each case methyl groups were being exchanged between the central nitrogen atoms.

In modifying the theory so as to eliminate the postulation of interchange of the amino-substituents, there are two alternatives. The postulate of coplanarity may be abandoned, in which case the rings are perpendicular (Fig. 2). The abandonment of this postulate is consistent with resonance theory, for coplanarity of resonating moieties is demanded only when partial double bond character is imposed on a bond owing to resonance interchange.

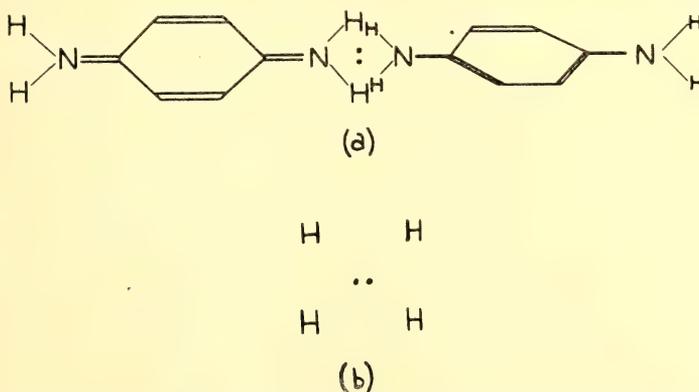


Fig. 2.—The axes of the two benzene rings are co-linear and the rings lie in mutually perpendicular planes. The imino-H atoms lie in the plane of the attached molecule; the amino-H atoms lie approximately in the plane of the Kekule ring. The four central H atoms lie approximately at the vertices of a square in a plane perpendicular to both rings.

Alternatively, the postulate of co-linearity of the benzene rings may be abandoned, in which case a limiting structure of the type shown in Fig. 3 would be expected.

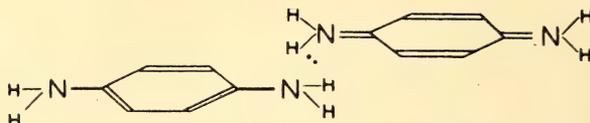


Fig. 3.—The axes of the two benzene rings are not co-linear, and the rings lie in parallel planes. The central H atoms lie approximately at the vertices of a square in a plane inclined to the rings.

RESULTS AND DISCUSSION.

1. δ -Salts of Fully N-substituted Diamines.

Michaelis and Granick obtained no "satisfactory" bromides or iodides of 1:4-(bis)-dimethylaminobenzene and Willstatter and Piccard (1908) also failed to obtain a reproducible bromide.

However, reasonably reproducible salts have now been obtained using these anions when certain factors were controlled, particularly the nature of the solvent.

Paramagnetic bromides and iodides of magnetic susceptibility close to that calculated for free radicals (monomeric semiquinone ions) with one unpaired electron, and also, under different conditions, salts with low susceptibility were obtained. These last-mentioned salts (γ -halides)² were obtained either by oxidation in methanol or aqueous methanol solution followed by precipitation with ether, or alternatively by oxidation in ether-methanol or dioxane solution. The γ -halides were brownish powders with a violet streak; they differed in appearance from the brilliant silky lustre of the paramagnetic salt.

Both types of salt altered rapidly (and irreversibly), on standing, to almost colourless compounds (ω -salts) of the same empirical formulae, but no longer giving the intense blue solution characteristic of Wurster's Blue³ when dissolved.

The relevant data for these salts are listed in Table I.

The oxidation levels, listed in Table 1, as measured by catalysed hydrogen uptake in Warburg manometers, indicate that both the paramagnetic and the γ -salts are on the first semiquinone level. The results suggest that separation of salts with low susceptibility is associated with a low dielectric constant of the precipitating medium.

The paramagnetic halides are identified as free radicals of 1:4-(bis)-dimethylaminobenzene. In order to account for the properties of the γ -salts, it will be necessary to assume one of the following: (a) That the γ -salt is a mixture of the s -form and the π -form. (b) That the γ -salt is a mixture of the s -form and the ω -form. (The hypothesis of incomplete bond formation, which has been advanced (Michaelis and Schubert, 1938) to account for the anomalous susceptibility of Kuhn and Ströbele's arabinoflavins (Kuhn and Ströbele, 1937), for example, is not considered here, as it is inconsistent with the all-or-none law for bond formation (Pauling, 1939).)

² Salts of anomalously low susceptibility are termed in this paper γ -salts.

³ Salts of the semiquinone ion derived from 1:4-(bis)-dimethylaminobenzene are called salts of Wurster's Blue.

TABLE I.

δ-Salts of 1:4-(bis)-dimethylaminobenzene.

Salt.	Oxidation Level. (H ₂ uptake in μ l/mg. at N.T.P.)		Solvent.	Magnetic Susceptibility. ($\chi_m \times 10^6$ c.g.s.)			T° C.
	Calculated.	Observed.		Calculated.		Observed.	
				Radical.	Dimer.		
s-Bromide ..	52.0	43.0	10% MeOH (a)	+1133	-154	+1040	16
γ -Bromide ..	52.0	46.0	MeOH, Et ₂ O (b) (ppd.)	"	"	+96	14
s-Iodide ..	31.0	21.0	10% MeOH	+1127	-160	+1004	16
γ -Iodide ..	31.0	24.0	MeOH, Et ₂ O (ppd.)	"	"	+51	16
ω -Bromide ..	(0)	0	(In vacuo)	—	-154	-142	15
ω -Iodide ..	(0)	0	(In vacuo)	—	-160	-138	17
s-K ₃ Fe(CN) ₆ ..	30.2	25.0	10% MeOH	+1158	-120	+1031	18
ω -K ₃ Fe(CN) ₆ ..	(0)	0	(In vacuo)	—	"	-131	17

Note.—(a) I.e., 90 volumes methyl alcohol and 10 volumes water.

(b) I.e., precipitated by ether from methyl alcohol solution.

Alternative (b), although unlikely, is listed as a possibility because of the rather large limit of error in the oxidation level determinations. However, the measurements were made immediately after preparation, and the rate of conversion to the ω -form was found to be too slow (even with the most unstable salts) to account for the low susceptibilities.

Alternative (a) is the more probable explanation of the anomalous susceptibilities. (This hypothesis was the alternative to that of partial bond formation originally advanced by Schwarzenbach and Michaelis (1938) to explain the low susceptibilities in the flavin series.)

Against this conclusion it might be claimed that the potentiometric examination of Wurster's Blue already published (Michaelis, 1931; Michaelis and Hill, 1933; Michaelis, Schubert and Granick, 1939) has failed to reveal any signs of dimerization in solution. This aspect of the problem will be discussed in a later paper; but it can be pointed out here that the published potentiometric work provides no conclusive evidence against the possibility of dimerization of the Wurster's Blue radical, since—

- (i) the potentiometric experiments published have been carried out in water or water-methanol, whilst the γ -salts have been obtained from either ether or dioxane solutions; and it is known that change of solvent has a marked influence on dimerization equilibria.
- (ii) The experiments on Wurster's Blue have been carried out at a dilution which has since been found to be unfavourable to dimer formation. (Michaelis and Schubert, 1938.)
- (iii) The parallel examination of the semiquinone ion of 1-amino:4-dimethylaminobenzene (Wurster's Red) (Michaelis, 1931) failed to reveal dimerization of the 1-amino:4-dimethylaminobenzene radical.

Included in Table 1 are data for the $K_3Fe(CN)_6^-$ salt of 1:4-(bis)-dimethylaminobenzene. (For remarks on the ferrocyanide series, see Section 2.) This salt is unstable, although immediately after preparation it exhibits the typical colour and lustre of the radical, it changes in a few days to the silvery-white ω -salt, with a χ_m close to the Pascal diamagnetic correction. This shows that paramagnetism of salts of the ferrocyanide series is not even in part due to the anion.

As another test of conclusions (2) and (3) of the Michaelis-Granick theory, δ -salts of 4:4'-(bis)-dimethylaminodiphenyl were isolated. The possibilities of resonance in the benzidine series are substantially the same as in the p-phenylene diamine series.

With the anions bromide and perchlorate, deep green powders were obtained on treatment with bromine, and these changed on standing in vacuo or in the air or on warming to a light yellow powder (presumed to be the ω -form). Methanol solutions of the green oxidation product do not change colour on cooling to $-40^\circ C.$, but, on warming to $50^\circ C.$ the colour reversibly changes to a light yellow; the process may be repeated many times. This looks similar to the typical dimerization phenomena of meriquinoid salts; however, the experiments of Lewis and Lipkin (1942) on photosensitized oxidation of 4:4'-(bis)-dimethylaminodiphenyl in rigid solvents indicate that the monomer of 4:4'-(bis)-dimethylaminodiphenyl is green, which suggests that the colour change is not due to dimerization. No explanation of this is offered. There is, however, the possibility that the amine is associated in the rigid solvent in Lewis' and Lipkin's experiments.

Complete analysis of the green bromide showed it to have the empirical formula $C_{16}H_{20}Br$; further, it was found that all the bromine present was ionizable, *i.e.*, there is no nuclear bromination.

In the ω -form the bromine was also ionizable.

Data for the bromide and perchlorate salts are given in Table 2.

TABLE 2.

 δ -Salts of 4:4'-(bis)-dimethylaminodiphenyl.

Salt.	Oxidation Level. (H ₂ uptake in μ l/mg. at N.T.P.)		Solvent.	Magnetic Susceptibility. ($\chi_m \times 10^6$ c.g.s.)			T° C.
	Calculated.	Observed.		Calculated.		Observed.	
				Radical.	Dimer.		
π -Perchlorate ..	37.5	34.1	10% MeOH	+1135	-152	-166	16
			20% MeOH	"	"	-170	15
π -Bromide ..	35.3	37.0	10% MeOH	+1128	-154	-173	17
	35.3	34.0	CHCl ₃	+1135	"	-170	16
			20% MeOH	"	"	-168	16
ω -Perchlorate ..	(0)	0	(In vacuo)	—	(-152)	-153	16
ω -Bromide ..	(0)	0	(In vacuo)	—	(-154)	-155	14

These results show that the salts are wholly diamagnetic and that the green form is on the first semiquinone level. They are thus identified as π -salts of 4:4'-(bis)-dimethylaminodiphenyl; again it would seem that a dimer has been formed even when the amino groups of the parent amine are completely substituted.

2. δ -Salts of Partially N-substituted Diamines.

In order to test conclusion (3) of the Michaelis-Granick theory, attempts were made to prepare δ -salts with anions other than bromide, iodide and perchlorate. Iodates, chromates and benzoates could not be isolated, but a series of ferrocyanides was obtained by the addition of aqueous potassium ferricyanide to aqueous methanol solutions of the free amine (sometimes saturated with potassium ferrocyanide). For the salts to be described, the reaction can be represented as $A + K_3Fe(CN)_6 \rightarrow AK_3Fe(CN)_6$. For purposes of comparison the perchlorates were also prepared.

Data for these salts are given in Table 3.

TABLE 3.
(a) δ -Salts of 1-Amino: 4-dimethylaminobenzene.

Salt.	Solvent.	Magnetic Susceptibility ($\chi_m \times 10^6$ c.g.s.).			T° C.
		Calculated.		Observed.	
		Radical.	Dimer.		
π -Perchlorate	10% MeOH	+1150	-128	-105	18
s-Ferrocyanide (a) ..	20% MeOH	+1173	-96	+1098	20
π -Iodide	10% MeOH	+1141	-146	-120	16
π -Bromide	10% MeOH	+1148	-130	-130	18

(b) δ -Salts of 1:4-Methylaminobenzene.

π -Perchlorate	10% MeOH	+1141	-128	-136	20
(s+w)-Ferrocyanide (b)	20% MeOH	+1182	-96	to +18	18
π -Iodide	10% MeOH	+1141	-146	-115	16
π -Bromide	10% MeOH	+1152	-130	-100	17

Note on Table 3.—a: This is the first paramagnetic solid salt of 1-amino,4-dimethylaminobenzene that has been described. A brief note by Pauling (1939) claims that in unpublished experiments by Pauling and Sturdivant a paramagnetic iodide of Wurster's Red was obtained. The formula given for the radical, however, is that of the salt of 1:4-(bis)-methylaminobenzene, which is not Wurster's Red.

We were unable to obtain anything but a diamagnetic iodide or bromide by oxidation of 1:4-(bis)-methylaminobenzene. Both salts are stable and the values of the magnetic susceptibility for the iodide and the bromide are in substantial agreement with the figures of Michaelis and Granick.

b: This salt had the usual semimetallic lustre of the paramagnetic salts, but changed very rapidly to the colourless (silvery) ω -form, which gives almost colourless solutions. It is evidently a very unstable radical.

The data for the perchlorates (Table 3) agree substantially with those published by Michaelis and Granick.

It is seen that the anion has a considerable influence on the state (σ - or π -) and stability of the precipitated salt. Whereas with the perchlorate a very stable free radical for the δ -salts of 4:4'-(bis)-methylaminobenzene and an unstable dimer for those of 1:4-(bis)-methylaminobenzene and 1-amino,4-dimethylaminobenzene are obtained, with the $\text{K}_3\text{Fe}(\text{CN})_6^-$ anion a very stable radical for δ -salts of 1-amino,4-dimethylaminobenzene and an unstable radical for δ -salts of 4:4'-(bis)-dimethylaminodiphenyl and 1:4-(bis)-methylaminobenzene are obtained.

3. δ -Salts derived from 4:4'-diaminodiphenyl (benzidine).

Since the beginning of the century several workers have investigated the structure of the oxidation products of benzidine. In particular, Barzilovsky (1905) and Schlenk (1908) have shown that these oxidation products are meriquinoid salts and all analyse according to an empirical formula, A_nX , where A is the positive cation derived from benzidine and X is an anion of valency n .

The bromide, perchlorate and ferrocyanide δ -salts of benzidine have been prepared and the data for these salts are listed in Table 4.

TABLE 4.
 δ -Salts of 4:4'-Diaminodiphenyl.

Salt.	Oxidation Level.		Solvent.	Magnetic Susceptibility ($\chi_m \times 10^6$ c.g.s.)			T° C.
	Calculated.	Observed.		Calculated.		Observed.	
				Radical.	Dimer.		
π -Perchlorate ..	—	—	10% MeOH	+1086	-201	-116	16
π -Bromide ..	48.1 (a)	44.0	10% MeOH	+1079	-203	-123	17
Ferrocyanide ..	4.0 (b)	4.1	MeOH susp.	—	-485	+685	16
Ferrocyanide ..	4.0 (b)	3.8	H ₂ O susp.	—	-485	+1290	15

Note.—(a) H₂ uptake in $\mu\text{l}/\text{mg}$. at N.T.P., measured manometrically.

(b) Oxidation level determined by method of Schlenk (1908).

Note to Table 4.—Consideration of the results of photosensitized oxidation of benzidine and its derivatives (first observed by Noack (1925) and discussed by Weiss and Fishgold (1936)) and of the early work on analysis of the salts led J. Weiss (1938) to maintain that the meriquinoid salts, which had been thus far described, were all positive benzidine-ion free radicals. This does not appear to be the case.

If the ferrocyanide salts are indeed of the semiquinone type, the variation in magnetic properties of these δ -salts could be explained in the same manner as the similar variation in the δ -salts of the p -phenylene diamine series. It must also be noted that the highest Bohr magneton number calculated for the ferrocyanides from the observed mean moments is less than half the value calculated by means of the van Vleck formula and the Curie law for the molecule Bz_4X , with four unpaired electrons.

SUMMARY.

The above results show the following:

(a) Solid *s*-salts (on the first semiquinone oxidation level) may be obtained from all the amines studied with the possible exceptions of 4:4'-(bis)-dimethylaminodiphenyl and 4:4' diaminodiphenyl.

(b) Salts, which are mixtures of the semiquinone ion and the dimerized form, can be obtained by suitable selection of conditions.

(c) By variation of the anion it is possible to prepare either paramagnetic or almost diamagnetic δ -salts of 1:4-(bis)-methylaminobenzene, 1-amino, 4-dimethylaminobenzene, 1:4-(bis)-dimethylaminobenzene and possibly 4:4'-diaminodiphenyl (benzidine).

If the restrictions of the Michaelis-Granick theory, which lead to the postulation of interchange between the central nitrogen atoms of the dimer of groups attached to them during the resonance cycle, are removed and a structure such as that shown in Fig. 2 or in Fig. 3 substituted for these, then the structural criterion for dimer formation will be *simply* whether or not the steric strain is sufficient to counterbalance the increase in resonance energy gained by dimerization. And there is no reason to suppose that this will be the case with derivatives of completely N-methylated diamines.

Parts (b) and (c) may be re-stated as follows:

Salts, which are a mixture of the radical and of the dimer, will be isolated only from solutions in which an equilibrium exists between these two forms, as well as the totally reduced and totally oxidized forms. Where such an equilibrium exists, the ratio of *s* to π in the salt formed with a specified anion will depend upon (i) the semiquinone dimerization and dimeric formation constants governing the equilibrium, and (ii) the relative solubilities of the salts of *s* and π with the anion.

The consequences of this hypothesis relevant to (b) and (c) are:

I. For any specified anion the magnetic moment of the salt (taken as a measure of the ratio *s*/ π) will vary if the solvent is changed and if the conditions of formation, which affect the values of the effective semiquinone, dimerization and dimeric formation constants (Michaelis and Schubert, 1938) are altered.

II. Variation of the anion will be expected to produce a change in susceptibility where other conditions are maintained constant owing to the fact that the solubility ratio S_s/S_π will vary for each anion. Confirmation is to be found by contrasting the halides with the $K_3Fe(CN)_6$ salt of 1-amino, 4-dimethylaminobenzene (Wurster's Red). The susceptibility of the halides is that of the dimer; of the ferrocyanide, that of the radical. Both types of salt are isolated from a deep blue solution, *i.e.*, from one which contains a large (if not predominant) proportion of dimer. It will be expected that in this case the *s*-ferrocyanide is less soluble than the π -ferrocyanide.

This hypothesis, if correct, might account for the numerous anomalously low susceptibilities cited in the literature, *e.g.*, for the arabinoflavins, and for Katz's dihydropyocyaninium and tetra-*p*-tolylhydrazinium perchlorates.

Finally, two further details of the Michaelis-Granick theory are open to question. Firstly, these authors, in their exposition of Pauling's all-or-none law, speak of the "assumption that no molecular collision resulting in chemical interaction can occur in the solid state" and deduce that "in the crystalline state only resonance, but no chemical reaction, occurs". The

all-or-none law, however, forbids only resonance between structures with different numbers of unpaired electrons, so inferences about the impossibility of a reaction cannot be drawn. In particular, the transition to the ω -form takes place in the solid state.

Secondly, from the fact that the rate of conversion of the π -form to the ω -form of a salt varies with (among other factors) the nature of the original amine, Michaelis and Granick conclude that the faster the rate of conversion, the weaker is the dimeric bond in the π -salt. This is untenable, as it involves a confusion of free energy with energy of activation.

EXPERIMENTAL.

Methods of Measurement.

Magnetic measurements were made by the Gouy method. All measurements were made at a current of 3 amperes, and the amount of material used for each determination was 0.4 gm. The weighing tube constants were determined by standardization with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The theoretical values for the magnetic susceptibilities of the δ -salts were calculated by means of the equation of Van Vleck (1932) and the unmodified Curie law. The structural, atomic and ionic diamagnetic contributions to molar susceptibilities values are based on the modified Pascal constants (c.f. Selwood, 1943) and those of Trew (1941). The values calculated for the theoretical diamagnetic susceptibility differ from those of Michaelis and Granick, presumably owing to the use of different values for the anionic diamagnetic susceptibility.

Oxidation level determinations were carried out by catalytic micro-reduction, using the Warburg constant volume manometers. The most efficient procedure was found to be the following: In each cup was placed a weighed amount (2-7 mg.) of the substance, a measured volume of solvent added, and a measured amount of catalyst placed in the side-arm. The solutions were first equilibrated and then the catalyst was mixed in. The usual manometric technique was employed; it was found that several blank experiments were required for each set.

Of catalysts employed, a colloidal palladium sol containing 1 gm. Pd per litre (prepared by the reduction of palladous chloride in the presence of gelatin) was the most efficient.

Raney nickel and colloidal Pd and Pt prepared by the Bredig method were either less active or gave unreplicable results.

The oxidation level was in one case (ferrocyanide salt of 4:4'-diaminodiphenyl) determined by macro-reduction using stannous chloride, after the method of Schlenk (1908).

PREPARATIONS.

δ -Salts of 1:4-(bis)-Dimethylaminobenzene.

Perchlorate: This was prepared from the amine hydrochloride according to the method of Michaelis and Granick (1943), and also from the free amine. The amount of bromine added (corresponding to 0.7 equiv.) was 50 mls. 0.025 N bromine per 2 gms. dihydrochloride, or per 1.4 gm. amine. The product was purified before measurements were taken by shaking with distilled water and filtering several times.

s-Bromide: A solution of 0.8 gm. of the free amine in 90% methanol was cooled to -10°C ., stirred slowly, and 0.7 equiv. bromine in 6 mls. methanol added dropwise. Stirring was continued for several minutes after completion of bromine addition; the solution was then filtered through sintered glass. The product was washed first sparingly with distilled water, then with methanol; finally it was washed abundantly with dry ether. The product consisted of brown needles with metallic lustre, which gave an indigo blue streak. Found: Br, 29.8%. Calculated for $\text{C}_{10}\text{H}_{16}\text{N}_2\text{Br}$: Br, 32.6%.

γ -Bromide: The oxidation was carried out with the same amount of bromine as for the *s*-bromide. The salt was either (a) precipitated from an 80% ether-methanol solvent or (b) precipitated by ether from an excess methanol solution. In each case the salt which separated possessed a low moment. The analysis recorded is for salts prepared by method (a). Found: N, 11.10; Br, 31.82%. Calculated for $C_{10}H_{16}N_2Br$: N, 11.06; Br, 32.60%.

s-Iodide: A 90% aqueous methanol solution of the free amine was treated with 0.7 equivalents of iodine in methanol solution at 0°C. The salt separated in long needles with a brilliant sub-metallic lustre. The iodide was more stable than the *s*-bromide. It was filtered off and purified as in the preceding methods. Found: I, 42.86%. Calculated for $C_{10}H_{16}N_2I$: I, 43.60%.

γ -Iodide: This salt was obtained by oxidation of the free amine with 0.7 equiv. iodine. As with the γ -bromide, two methods were followed: (a) the oxidation was carried out in 80% ether-methanol, from which the salt separated, or (b) the salt was precipitated from an excess methanol solution by ether. The product was purified as before, and did not possess the needle form or the lustre of the corresponding *s*-salt. The analysis recorded is that of the salt prepared by method (b). Found: C, 41.60; H, 5.60; I, 42.70%. Calculated for $C_{10}H_{16}N_2I$: C, 41.24; H, 5.53; I, 43.60%.

Ferrocyanide: This was prepared from the free amine in aqueous methanol solution. The solution was cooled to 0°C. and 0.7 equivalents aqueous potassium ferrocyanide (in 1 ml.) pipetted in slowly with stirring. The salt, which separated from the intensely blue solution exhibited the needle form, brown colour, sub-metallic lustre and blue streak characteristic of paramagnetic Wurster's Blue salts. The salt was unstable and changed to the light green hygroscopic ω -form in a few days. Found: N, 22.63%. Calculated for $C_{16}H_{16}N_8FeK_3$: N, 22.70%. The ω -form of this salt was analysed for nitrogen, but the figure is not thought to be accurate owing to the extremely hygroscopic nature of the salt. Found: N, 21.50%. Calculated for $C_{16}H_{16}N_8FeK_3$: N, 22.7%.

δ -Salts of 1-Amino-4-dimethylaminobenzene.

Ferrocyanide: An aqueous methanol (10% MeOH) solution of the free amine was cooled to -5°C., and 0.7 equiv. potassium ferricyanide dissolved in the minimum amount of distilled water, was run in from a pipette with constant stirring. The green salt, which separated from an intensely blue solution, was filtered over sintered glass, and washed sparingly with methanol, distilled water, and dry ether. The dry salt exhibited a brilliant sub-metallic lustre under the microscope, gave deep red dilute solutions and deep blue concentrated solutions. The salt was stable for months. Found: C, 35.83; H, 2.61; N, 26.03%. Calculated for $C_{14}H_{14}N_8FeK_3$: C, 36.12; H, 2.60; N, 24.08%.

The bromide, iodide and perchlorate of this amine were prepared both (1) from the hydrochlorides, after the method described by Michaelis and Granick (1943), and (2) from the free amine. No difference was observed between salts prepared by the two methods.

δ -Salts of 4:4'-(bis)-Dimethylaminodiphenyl.

Perchlorate: To a solution of 100 mls. 90% aq. methanol containing 10 gms. sodium perchlorate, 0.4 gm. 4:4'-(bis)-dimethylaminodiphenyl dihydrochloride were added. The clear solution was filtered and cooled to -5°C.; then 9.6 mls. 0.103 N aq. bromine were added dropwise with vigorous stirring. The precipitate was filtered and formed a deep blue filter cake, which dried to a deep green. It was washed abundantly with distilled water, methanol and dry ether. Yield: 0.3 gm. Found: N, 8.18%. Calculated for $C_{16}H_{20}N_2ClO_4$: N, 8.25%.

Bromide: To a solution of 810 mls. methanol was added 2.92 gms. of the dihydrochloride, and 120 mls. of an aq. solution of sodium bromide (containing 30 gms. NaBr) stirred in. After cooling to -5°C., 70 mls. 0.095 N aq. bromine were added dropwise

with stirring. The bluish precipitate was collected and treated as above. The filtrate was straw yellow. Yield: 2.5 gms. Found: N, 8.75; Br, 24.96%. Calculated for $C_{16}H_{20}N_2Br$: N, 8.65; Br, 24.68%.

Ionizable bromine analyses were carried out on both the green bromide and the ω -bromide. 0.15 gm. samples were used in each case.

	NaOH Neutralization Observed.	NaOH Neutralization Calculated (for 1 equ. bromide/320 gms.).
Bromide	0.0186 gm.	0.0188 gm.
ω -Bromide	0.0181 gm.	0.0188 gm.

δ -Salts of 4:4-Diaminodiphenyl (Benzidine).

Bromide: To a solution of sodium bromide (50 gms.) in 1 litre methanol was added benzidine (2 gms.); this was stirred until completely dissolved and the solution filtered. The filtrate was cooled to -10°C ., and 72 mls. of 0.106 N aq. bromine added dropwise with constant stirring. The blue suspension was filtered, washed abundantly with distilled water, methanol and dry ether. The product was a deep indigo blue powder, apparently amorphous. Yield: 1.6 gms. (The temperature of the preparation was varied and the magnetic susceptibility of the product was not altered until a temperature of about 50°C . was used.) Found: C, 54.48; H, 4.78; N, 10.10; Br, 29.31%. Calculated for $C_{12}H_{12}N_2Br$: C, 54.56; H, 4.58; N, 10.60; Br, 30.26%.

Perchlorate: An exactly similar method was used, with sodium perchlorate in place of sodium bromide. Yield: 1.8 gms.

Ferrocyanide: (1) 3 gms. finely powdered benzidine were suspended in 330 mls. distilled water and vigorously stirred. A solution of 3.6 gms. potassium ferricyanide in 18 mls. water was added dropwise to the suspension over a period of half an hour. The stirring was continued for a further half-hour, after which the blue suspension was filtered through sintered glass. The filter cake was washed abundantly with cold distilled water, then with absolute ethanol until the bromine test showed all unchanged benzidine had been removed; finally it was washed with dry ether.

(2) The same method was followed except for the use of methanol or methanol-water mixtures for the suspending liquid.

(3) Benzidine dihydrochloride in aqueous solution was used.

Found: C, 65.14; H, 5.19 (using preparation from method (1)); N, 21.20% (from method (2)); and N, 21.50% (from method (3)). Calculated for $C_{64}H_{48}N_{14}FeK_3$: C, 68.34; H, 5.09; N, 21.11%.

The filtrate from the preparation of bromide was almost colourless; that from the ferrocyanides was light green, darkening markedly on standing.

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DETERMINATION OF MAXIMUM INHERENT MOISTURE IN COAL BY CONTROLLED VAPORISATION OF ADHERENT MOISTURE.

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INTRODUCTION.

The rôle of inherent moisture in coal, its relations to micelle structure and rank, and difficulties in determination of its maximum values have been reviewed in recent papers by Dunningham (1943), Bangham (1943) and King and Wilkins (1943).

The total moisture content of freshly-mined coal consists of *inherent moisture* held by capillary condensation or adsorption on the internal surface (or intermicelle spaces) of the coal substance, as well as *adherent moisture* which may be present on the external surface of the coal and in cracks and internal cavities too large to be considered part of the structure of the coal substance.*

Inherent moisture is distinct from adherent moisture in so much that its vapour pressure is lowered by the small diameter of the spaces in which it is adsorbed. *Maximum inherent moisture* is that which coal contains when all capillary spaces are filled with adsorbed moisture but no adherent moisture is present. In its original condition in the seam, coal usually contains its maximum inherent moisture content together with a variable quantity of adherent moisture which is really ground-water lying, or circulating, in the seam and associated strata. In well-drained strata outcropping on hillsides there may be very little adherent moisture in the seam, and in some cases it appears that the total moisture content may be less than the maximum inherent value.

When freshly mined, coal contains approximately the same amount of moisture as in the seam. When delivered to the consumer, the moisture may be much lower if the coal has been exposed to dry air which removes adherent moisture and part of the inherent moisture. If the coal has been washed in preparation for marketing, or exposed to rain during transport and storage, adherent moisture may have been added, giving a total moisture content higher than the original value.

The total moisture content of coal, as mined or at any subsequent stage, is readily determined by drying a representative sample at 105° C. in dry nitrogen. Moisture contents obtained in this way are required for industrial purposes, but they are of little value in scientific work when the fundamental properties of coal are to be compared or studied in relation to the structure of the coal substance. Moisture contents on the "air-dried" basis have been used in the

* The terms *adherent* and *inherent* are used in this paper to describe those portions of the total moisture content possessing normal and sub-normal vapour pressure respectively. In some brown coals, which have suffered but little compression and in which cleat has not developed, a considerable portion of the natural bed-moisture may be contained in openings too large to lower the vapour pressure of water, but which form an essential part of the coal structure, as pointed out by Dr. A. B. Edwards and Mr. J. R. Bainbridge, Melbourne University (private correspondence).

past for scientific purposes, but they are unsatisfactory as the amount of inherent moisture varies with relative humidity of the atmosphere in which the coal is dried. Results obtained by drying coal at constant humidity have also been used, but they are of no true value as they only indicate the amount of moisture held in capillaries of radii equal to, or smaller than, those capable of retaining water at the particular humidity employed.

For scientific work, including classification of different coals, results of true value are those based on maximum inherent moisture content. To obtain this it is necessary to make sure that all capillary spaces are completely filled with adsorbed water. This condition exists in coal sampled at a fresh damp face in underground workings but adherent moisture, also present, gives a total moisture content in excess of the maximum inherent value. When the fresh working face is not obviously damp, very little adherent moisture is present and unavoidable drying during crushing, sieving and handling in the laboratory may remove part of the inherent moisture, resulting in a content lower than the maximum inherent value. To avoid this, and to ensure that maximum inherent moisture is present, it is usually necessary to add water to the coal when sampled and to keep it wet during subsequent handling. If a little inherent moisture is lost by air-drying, the coal can be resaturated by immersing in water, or by standing in saturated atmosphere, for a prolonged period. While standing in saturated atmosphere the capillaries slowly fill with inherent moisture, and adherent moisture condenses and accumulates on the coal and in cracks.

It follows that determination of maximum inherent moisture depends on complete removal of adherent moisture from saturated coal without removing any inherent moisture from the coal substance, or on complete filling of capillaries with inherent moisture without allowing adherent moisture to collect on the coal. Once this is accomplished, maximum inherent moisture can be determined merely by drying the coal at 105° C. in dry nitrogen.

PREVIOUS METHODS USED IN DETERMINATION OF MAXIMUM INHERENT MOISTURE.

Methods previously available for determination of maximum inherent moisture are as follows (see also Dunningham, 1943):

1. By plotting the adsorption curve for the coal up to the equilibrium moisture content at about 90% relative vapour pressure, and then extrapolating to 100%. This is unsatisfactory owing to the large degree of uncertainty regarding the form and position of the curves where they approach 100% saturation.

2. By exposing partially air-dried coal to saturated atmosphere until adsorption is complete, and then determining the moisture content. This method usually gives results which are too high and which cannot be satisfactorily reproduced, as adsorption is slow and adherent moisture commences to accumulate before the process is complete and continues until droplets of water can be seen on the coal.

3. By exposing wet coal (sample with excess adherent moisture) to unsaturated atmosphere until all adherent moisture is removed by evaporation. This is unsatisfactory, as complete removal of adherent moisture from cracks and inner cavities cannot be judged from the appearance of the coal, and it is probable that loss of inherent moisture commences before all the adherent moisture is removed.

4. The United States Bureau of Mines, Pittsburgh Experimental Station (1945), recently described a method for "Determination of Coal Surface Moisture" (i.e. adherent moisture) by placing a weighed quantity of wet coal in alcohol for a short (standardized) period of time then rapidly filtering off the

alcohol and determining the amount of water dissolved by change in specific gravity. This method was primarily designed for rapid determination of adherent moisture in coal for by-product coke ovens; in connection with bulk density and angle of repose of crushed coal; and as a routine check on efficiency of dewatering in coal washeries. It could be used for determination of maximum inherent moisture by first determining total moisture in the wet coal, and then adherent moisture removed by solution in alcohol—the difference between the two being the maximum inherent moisture. The results, however, would be relative, depending on length of time the coal remained in the alcohol, as inherent moisture is also removed from coal by solution in alcohol (Dulhunty, 1946). Furthermore, extraction time would have to be varied for coals of different rank and results may not be comparable.

5. A method devised by Dunningham (1943) in which adherent moisture is removed from wet coal by adsorption in blotting paper. The wet coal is shaken in a bottle lined with dry blotting paper, then transferred to another bottle, and the treatment repeated several times until the blotting paper remains dry, after which inherent moisture is determined by drying at 105° C. The method is standardised by using a given quantity of wet coal, crushed to a certain size, and by shaking for definite periods in bottles of given capacity for a certain number of times.

This is a simple, rapid and reliable method giving results which can be reproduced satisfactorily. It is suitable for industrial purposes and can be used in scientific work as demonstrated by Dunningham's results in the study of inherent moisture in coal. It would appear, however, that the blotting paper method has certain limitations. The results are relative rather than absolute as the amount of drying is standardised at that which appears to remove all adherent moisture. Short time of contact with dry blotting paper removes adherent moisture from the outer surface of coal particles, but not necessarily from all cracks and cavities, larger than capillaries, situated within the coal. Sufficient drying to remove all adherent moisture would possibly result in removal of some inherent moisture. The present writer found that coals of about the same rank and type can be satisfactorily compared by the blotting paper method, but different amounts of drying must be adopted for coals varying widely in rank and texture. Medium to high rank coals with compact texture require far less drying than low rank materials such as peat and brown coal of spongy, or fibrous, nature containing an abundance of internal cavities much larger than capillaries in the coal substance. It follows that results obtained for coals of different rank, requiring different amounts of drying, cannot be considered strictly comparable.

CONTROLLED VAPORISATION OF ADHERENT MOISTURE.

General Principles.

This method was developed with the object of obtaining results approximating to absolute values by a process which could be used, without variation in technique, for determination of maximum inherent moisture in coals of all rank and texture from peat to anthracite.

The method takes advantage of the fact that vapour pressure of inherent, or capillary-held, moisture is sub-normal, whilst that of adherent, or free, moisture is normal. It is based on the general principle that if wet coal is maintained at a constant temperature in an atmosphere of water vapour, or saturated air and water vapour, under a pressure which will just vaporise water at that temperature, adherent moisture with normal vapour pressure will pass to vapour, but inherent moisture with sub-normal vapour pressure will remain in the coal and can be determined by drying at 105° C. in the usual manner.

This principle offers the following advantages in determination of maximum inherent moisture. (i) Separation of adherent and inherent moistures depends on the difference in vapour pressure of the two, and the amount of moisture remaining in the coal, to be determined as maximum inherent moisture, is directly related to the total volume of capillary spaces capable of lowering the vapour pressure of water. It follows that results approximate to absolute values, and that they can be used in comparing moisture properties of coals of all rank and texture and for studying relations to physical and chemical rank-variation. (ii) The vaporisation process can be continued indefinitely until all adherent moisture is removed, without loss of inherent moisture as this is in contact with water vapour, or saturated air and water vapour, at a pressure higher than its vapour pressure. (iii) Adherent moisture is completely removed from all cracks and inner cavities as well as from the outer surfaces of coal particles. (iv) Adherent moisture is vaporised relatively quickly and a definite end-point is reached after which no more water is removed from the coal. This was established by plotting curves for moisture content at intervals during, and after, removal of adherent moisture. The process of vaporisation requires from six to eight hours, but apparatus can be designed to treat any desired number of coal samples simultaneously, enabling a large number of determinations to be carried out in a relatively short time. (v) The process can be carried out at any temperature from 100° C. to room temperature. The pressure required to cause vaporisation varies with the temperature employed. Results obtained by determinations on duplicate samples at different temperatures agree very closely. It is desirable to adopt a relatively low temperature as prolonged heating in the vicinity of 100° C. may cause physical changes in the micelle structure of some low rank coals, resulting in a reduction of internal surface and maximum inherent moisture. The most satisfactory temperature is one a little above the maximum temperature likely to be encountered in the laboratory, as it simplifies constant temperature equipment, enables the use of rubber fittings in the apparatus, and the coal is not heated appreciably.

Apparatus.

Apparatus suitable for controlled vaporisation of adherent moisture is illustrated diagrammatically in Figure 1. It consists of a glass tank or water-bath fitted with a mechanical stirrer and suitable equipment for maintaining constant temperature ($\pm 0.01^\circ$ C.) at about 30° C. A Beckmann thermometer is used for recording temperature. That part of the apparatus referred to as the pressure distributor carries a number of coal-tubes and is wholly immersed in the water-bath. It is connected by means of glass and rubber tubes to a saturated-air inlet valve, manometer and reduced-pressure control valve.

A pump is required, capable of reducing pressure to at least 5 mm. of Hg lower than the vapour pressure of water at the temperature of the water-bath. The pump is connected to the pressure control valve, which may be a manually operated needle valve, or an automatic control valve, by means of which any desired pressure can be maintained in the distributor and coal-tubes. The manometer connected to the distributor should be suitable for reading pressures accurately to 0.1 mm. of Hg. The saturated-air inlet valve is a small needle valve by means of which a very slow stream of air is allowed to enter the distributor under reduced pressure.

The distributor consists of a glass cylinder ($3\frac{1}{2} \times 1\frac{1}{4}$ in.) closed at both ends by rubber stoppers and divided into upper and lower compartments by a rubber partition. Ten coal drying-tubes ($3 \times \frac{1}{2}$ in.) fitted with rubber stoppers are attached to ten copper tubes ($1\frac{1}{4} \times \frac{1}{16}$ in.) which pass up through the base of the distributor into the lower compartment. The lower compartment communicates with the upper by means of a glass tube ($\frac{3}{32}$ in.) which passes up through the

rubber partition and extends to a position near the top of the upper compartment. The saturated-air inlet tube ($\frac{1}{8}$ in.) passes down through the top of the distributor to within $\frac{1}{8}$ in. of the base of the upper compartment. The tube ($\frac{1}{8}$ in.) leading to the pressure control valve passes into the top of the upper compartment. The tube ($\frac{1}{8}$ in.) from the manometer passes down through the top of the distributor, and the rubber partition, into the lower compartment.

When the apparatus is in operation, the upper compartment of the distributor is half filled with water. Air passing through the inlet valve is saturated at room temperature and pressure by bubbling through water before entering the valve. On entering the distributor it bubbles up through the water in the upper compartment and becomes saturated at the temperature and pressure maintained in the apparatus and coal-tubes. The slow stream of air helps considerably in maintaining constant reduced pressure in the system—particularly if a manually operated pressure control valve is used. Water vapour coming from the wet coal in the tubes passes into the lower compartment of the distributor, from which it displaces most of the air and then passes into the upper compartment, to be drawn off with saturated air through the pressure control valve. Small fluctuations in temperature or pressure may cause vapour and air to pass back into the lower compartment or even into the coal tubes. Any air which passes back in this way is saturated at the temperature and pressure in the coal tubes, and it cannot cause evaporation of inherent moisture.

Method.

Granular coal ($\frac{1}{8}$ to $\frac{1}{32}$ in.) is required for the determination. The coal must be thoroughly saturated with water to ensure that all capillary spaces are filled. If results are to correspond to maximum inherent moisture, as in the original seam-condition, fully air-dried coal should not be resaturated and used for the determination as irreversible changes in physical structure are likely to occur when coal is allowed to reach equilibrium moisture content at relative humidities lower than about 85%. Slightly air-dried coal, in which moisture has not fallen below the equilibrium content at about 90%, can be resaturated by immersing in water for at least seven days. The most satisfactory material is that to which water has been added immediately after sampling at a fresh face in underground workings and kept wet during subsequent handling in the laboratory. When prepared for moisture determination, the granular sample should contain a sufficient excess of adherent moisture to wet the inner surface of the coal tube, when filled, and produce small drops of water at points of contact between the coal grains and the glass. The drops appear as small dark spots on the wall of the tube owing to reflection effects at the curved surface of the glass.

The coal tubes, containing wet samples, are attached to the copper tubes on the distributor and the upper compartment is half filled with water. The distributor and coal tubes are then placed in the water-bath and connections are made to manometer, air inlet valve, and pressure control valve.

As a preliminary to the actual drying or vaporisation process, it is necessary at this stage to determine the "equilibrium pressure" at which neither vaporisation nor condensation of water occurs in the coal tubes at the particular temperature setting adopted on the Beckmann thermometer, as vaporisation is carried out at a pressure 0.3 to 0.4 mm. of Hg lower than the equilibrium pressure. This determination need not be made in subsequent dryings carried out at the same temperature if the mercury setting in the Beckmann is not disturbed.

To determine the equilibrium pressure, the water-bath is brought to the temperature selected on the Beckmann in the vicinity of 30° C. When temperature is steady ($\pm 0.01^\circ$ C.), the pressure control valve, connected to the pump, is opened and pressure in the distributor is reduced to within about 10 mm. of

the theoretical vapour pressure of water at the temperature of the water-bath and the air inlet valve is opened so as to allow a slow stream of air (about 40 bubbles per minute through the water in the distributor) to enter the system. Pressure is then reduced very slowly until adherent moisture just commences to vaporise as indicated by disappearance of excess moisture from the inner surfaces of the coal tubes, and slow reduction in size and number of the dark spots of water at points of contact between coal grains and the glass. This pressure

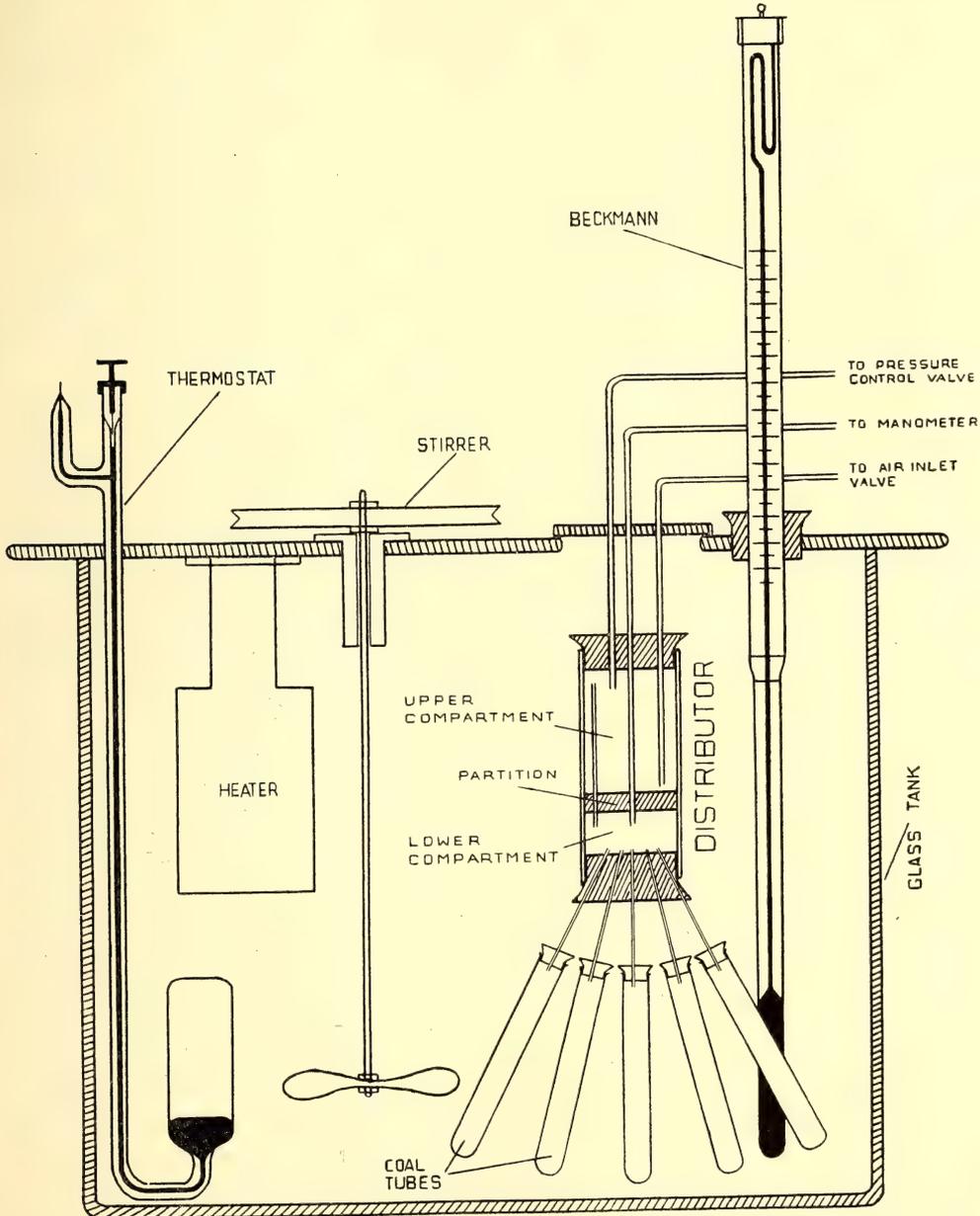


Fig. 1. Apparatus used for Vaporisation of Adherent Moisture.
(Five of the ten coal tubes are shown in diagram.)

is maintained (± 0.1 mm. indicated on the manometer) for about 20 minutes, after which time sufficient adherent moisture has vaporised to replace most of the air from the coal tubes and the lower compartment of the distributor. Pressure is then increased slowly until vaporisation ceases and condensation just commences as indicated by the appearance of dew on the inner surfaces of the coal tubes and a slight increase in size and number of the dark spots of water. Pressure is then reduced until vaporisation just commences again. After repeating this operation several times it is possible to determine the equilibrium pressure at which neither vaporisation or condensation occurs.

Having made the foregoing determination, vaporisation of adherent moisture is then carried out by reducing pressure to a manometer reading corresponding to 0.3 mm. to 0.4 mm. below the equilibrium pressure. This pressure is maintained until all traces of visible adherent moisture have disappeared from the coal tubes, which may require from one to four hours, depending on the amount of excess adherent moisture present in the first place. The process is continued for about three hours after removal of visible moisture to ensure vaporisation of all adherent moisture from cracks and inner cavities in the coal. Finally, pressure is increased by closing the pressure control valve, disconnecting the pump, attaching a water-bubbler, and allowing the distributor and coal tubes to fill with saturated air through the control valve. If removal of adherent moisture is not complete, dark spots of water will reappear when pressure is increased, and the process must be continued for an additional period.

When vaporisation of adherent moisture is complete, the coal tubes are removed from the distributor and the granular samples are transferred to glass-stoppered weighing bottles, previously weighed after filling with dry nitrogen at 105° C. This must be carried out without allowing the coal to come into contact with laboratory air which causes loss of inherent moisture by evaporation. It can be conveniently accomplished by using weighing bottles with necks of about the same diameter as the coal tubes. Each coal tube is disconnected from the distributor by withdrawing from the copper tube. The glass stopper is then removed from the weighing bottle as the rubber stopper is taken out of the tube, which is immediately placed against the neck of the bottle and inverted to run the coal down into the bottle. The tube is then removed as the glass stopper is replaced, and the bottle is weighed with the coal. (The transference of coal from tube to bottle need not be quantitative, as percentage of inherent moisture is determined in the coal actually transferred. Thus small particles of coal adhering to the inner surface of the tube may be neglected.) After weighing, the stoppers are removed from the weighing bottles, which are placed in an oven heated at 107° to 108° C. and a stream of dry nitrogen is introduced into each by means of a tube passing down through the neck to a position just above the surface of the coal. Oven drying by this method can be continued without danger of oxidation until the weight of dry coal is constant. Maximum inherent moisture is then calculated from loss of weight on oven drying, and expressed as a percentage of the weight of dry coal remaining in the weighing bottle.

Results.

At the equilibrium pressure, atmosphere in contact with the coal is approximately saturated. The pressure adopted for the determination (0.3 mm. to 0.4 mm. lower than the equilibrium pressure) was found in practice to be the pressure which would just cause vaporisation of adherent moisture at about 30° C. This means that the results correspond to equilibrium moisture contents at about 99% saturation. It does not appear possible to obtain results at full saturation, as adherent moisture is not removed and, theoretically, under such conditions inherent moisture would be infinitely great if sorption curves are

truly asymptotic to the 100% saturation line. The results, however, are believed to represent a close approximation to moisture content at full saturation which, for practical purposes, may be regarded as the conditions under which all capillaries forming part of the structure of the coal substance are completely filled with adsorbed water.

Variation of inherent moisture with pressure, under the conditions of determination, depends on the form of the sorption curves which probably vary considerably for different coals in the vicinity of 99% saturation. This factor influences the amount of error due to small fluctuations in temperature and pressure. Accurate data have not yet been obtained for pressure sorption relations above about 95% saturation, but it is hoped that this may form the subject of further investigation.

It follows that reproducibility of results depends on the form of the sorption curves, efficiency with which constant temperature and pressure are maintained during the vaporisation process, and accuracy with which moisture is determined by oven drying in the final stage. Also, as pointed out by Dr. D. H. Bangham (private correspondence), difficulty in avoiding small temperature gradients in the system, and the influence of the "hydrostatic level on pressure", may introduce error owing to the extreme experimental difficulty in exposing a macroscopic object to an atmosphere of uniform saturation.

Results in triplicate for a series of nine coals representing a wide range in rank and moisture content are given in Table I. The majority of coals give results which can be reproduced quite satisfactorily. Variations between duplicate determinations usually amount to less than 1.0% when expressed as maximum percentage deviation from the mean of the results, as illustrated by samples 1, 2, 3, 4, 6 and 8 in the table. With some coals it is more difficult to obtain close agreement between duplicate results, and percentage deviation may be somewhat higher, as in the case of samples 5, 7 and 9, which were included in the table to illustrate this feature. Such variation may be related to the form of the sorption curves where they approach a relative vapour pressure of 100%. In all cases, however, the actual variations between duplicate moisture values are relatively small compared with the total moisture contents and the large differences in moisture for coals of different rank.

TABLE 1.

Reproducibility of Maximum Inherent Moisture Determinations.

Coal Sample.		Rank.	Carbon A.F.D. Basis.	Triplicate Results.			Mean Value.	Varia- tion.	Max. % Deviation from Mean.
No.	Locality.			Max. 1	Inher. 2	Moist. 3			
1	Yallourn, Vic.	Brown coal.	68.4	80.20	80.70	81.60	80.83	1.40	0.95
2	Leigh Ck., Sth. Aust.	Brown coal.	71.9	54.70	54.30	54.50	54.50	0.40	0.33
3	Leigh Ck., Sth. Aust.	Sub-bitumen.	74.5	46.85	46.75	46.30	46.63	0.55	0.71
4	Collie, West. Aust.	Sub-bitumen.	74.8	20.20	20.40	20.15	20.25	0.25	0.74
5	Blair Athol, Q'land	Low - rank bitumen.	79.2	15.45	16.30	16.31	16.02	0.86	3.51
6	Wonthaggi, Vic.	Med. bitumen.	82.06	10.79	10.89	10.85	10.84	0.10	0.46
7	Borehold Seam, N.S.W.	Med. bitumen.	81.3	5.22	5.25	5.14	5.20	0.11	1.15
8	Greta Seam, N.S.W.	Med. bitumen.	80.8	3.06	3.07	3.02	3.05	0.05	0.98
9	Bullii Seam, N.S.W.	High - rank bitumen.	90.0	1.76	1.70	1.77	1.74	0.07	2.31

From the results in Table I it does not appear as though there is any close relationship between the amount of variation in actual values for duplicate results and the magnitude of the moisture content. Samples 5, 4 and 2, containing 16.02%, 20.25% and 54.50% of moisture, gave variations of 0.86,

0.25 and 0.40 respectively. There is, however, a general tendency for coals with highest moisture to give the greatest variation, and those of lowest moisture to give the smallest variation, as seen in the fact that samples 1, 2 and 3 with over 40% moisture gave variations of 0.4 to 1.4, while samples 7, 8 and 9 with less than 6% moisture gave variations of 0.11 to 0.05.

Improvements or modifications to the apparatus and method may give results which can be repeated with less variation, but the degree of reproducibility already attained is as satisfactory as in methods previously available for determination of maximum inherent moisture. In addition, the results are believed to approximate to absolute values for coals of all rank and texture, and they may be used to advantage in comparing moisture properties of different kinds of coal, or in studying relations between maximum inherent moisture and physical and chemical rank variation.

The controlled vaporisation method—designed primarily for scientific research on fundamental properties of coal—is somewhat complicated and requires specialised apparatus. For this reason it may not be suitable for routine moisture determinations in industrial work where a simple rapid method is required to deal with large numbers of coal samples of about the same rank and type, but in this connection it may provide a means of standardising the amount, or time, of drying in the more simple methods so as to obtain results approaching true or absolute values.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge the assistance of Dr. D. H. Bangham (B.C.U.R.A., London), who kindly read the manuscript and offered valuable suggestions regarding theoretical consideration of results; helpful discussion with Dr. T. Iredale (Department of Chemistry, University of Sydney) during experimental work and preparation of results for publication; the assistance of Miss N. Hinder, B.Sc., in laboratory work.

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A MAGNETIC SURVEY IN THE VICINITY OF THE VOLCANIC NECK AT DUNDAS, N.S.W.

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With Plate II and six Text-figures.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The Dundas volcanic neck is situated in the Parish of Field of Mars, County of Cumberland, about three miles to the north-east of Parramatta and about twelve miles north of west from Sydney. The position is shown on the Locality Plan, Fig. 1. The material of which it is composed has been

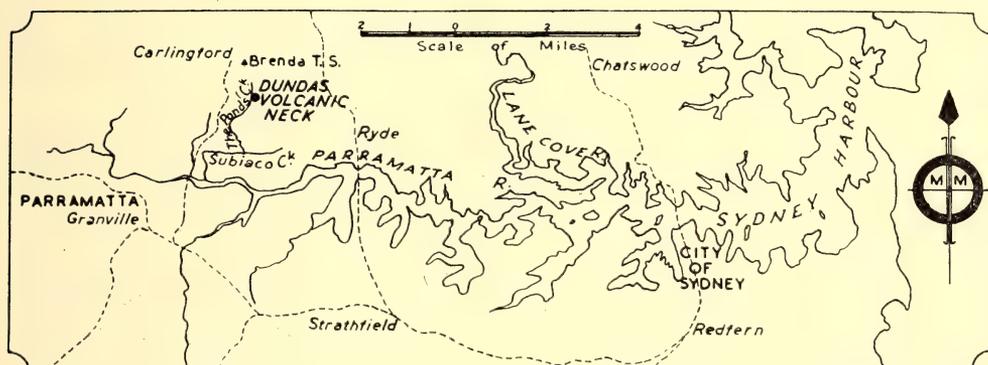


Fig. 1.—Locality Plan.

quarried intermittently during more than 100 years, the excavation now having a maximum length of about 500 feet, width of about 300 feet and being over 130 feet deep. Descriptions of the quarry at various stages of its working have been made by Clarke (1865), Wilkinson (1879) and Benson (1910). Photographs of it taken in 1940 are shown on Plate II.

The work described in this paper was undertaken in 1940-1 to determine whether there were associated with the neck any dykes or other masses of igneous material which were outside the limits of the present quarry. The results were analysed at that time, but were not arranged in a form suitable for publication. Recently it was considered that it may serve a useful purpose to place the results on record, and the present paper has been compiled with this purpose in view. A recent visit has disclosed that since the quarry was surveyed the shape of the floor had been considerably altered by subsequent quarrying operations. The middle bench has now been excavated almost to the same depth as the bottom bench. The floors of both benches were covered by water at the time of the visit and could not be inspected.

The writer wishes to extend his sincere thanks to Mr. J. M. Rayner, B.Sc., F.Inst.P., for his advice throughout all stages of the work and his assistance in obtaining from the Aerial, Geological and Geophysical Survey of Northern Australia the loan of the magnetometer used on the survey; and to his sister, Heather Hanlon, who assisted with most of the instrumental work in the field.

Technical Details.

The base plan, shown in Fig. 2, was surveyed by means of a plane table and telescopic alidade. Approximate heights above sea level are shown by contours, the interval on the undisturbed land surface being 10 feet and in the quarried area 20 feet. The relative heights between points as determined from contours are reasonably accurate, but the relationship of the base station A to sea level has been determined by aneroid readings only.

The magnetometer traverses were laid out on a north-south and east-west grid, the base station for the grid being at B. Magnetometer readings were mostly made every 20 feet along the traverses, although readings as close as 4 feet apart were taken in some critical areas. Readings were made at over 530 different stations, the positions of which are shown on Fig. 3.

Magnetic observations were carried out with a Schmidt type vertical magnetometer, Instrument No. 16128, constructed by E. R. Watts and Son, Ltd. The scale value was 34.9 gammas per division. The instrument was compensated for temperature changes, so that no temperature correction was necessary. Diurnal variation corrections were estimated from repeated check readings at base stations.

No determinations of absolute vertical intensity were made. Base station B was chosen as being representative of the normal vertical intensity throughout the area, in places undisturbed by the presence of basalt or other magnetic material. All values of vertical intensity shown on Fig. 3 are relative to this station.

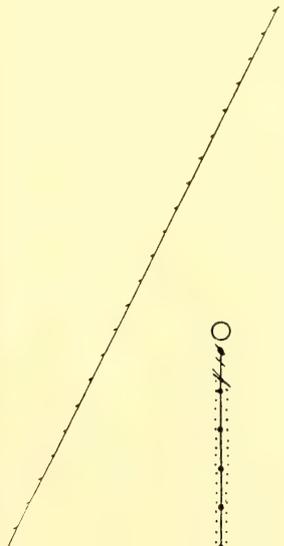
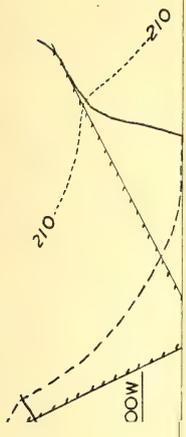
Throughout this paper the anomalies referred to and plotted as positive would be regarded as negative and vice versa by operators used to working north of the magnetic equator.

Geology and Topography.

The neck consists of a mass of breccia and basalt of Tertiary age, which has intruded shales of the Lower Wianamatta Series (Triassic) and underlying formations. The geology has not been shown on the plan of the area, Fig. 2, because the conventions used would have obscured other details shown. It may be taken, however, that the quarry area practically defines the limits of the main intrusion. The remainder of the area consists of Wianamatta shale, but in most parts the rock is obscured by a cover of soil. Some details of the geology can be seen in the photographs on Plate II. Petrological descriptions of the basalt, breccia and plutonic inclusions found in the neck have been made by Benson (1910).

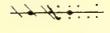
The neck occupies a hollow, open to the south. The greatest slope is towards the north, rising nearly 300 feet in about $\frac{3}{4}$ mile to Brenda Trigonometrical Station. The Ponds Creek rises to the north and then flows in a channel along the western edge of the quarry. Finally it joins Subiaco Creek, which flows into the Parramatta River (see Fig. 1). The courses of the tributaries of The Ponds Creek show a very close relationship to the areas which the magnetometric survey indicates would be underlain by basalt, as shown on Fig. 2. Portions of the beds of the creeks are overgrown with

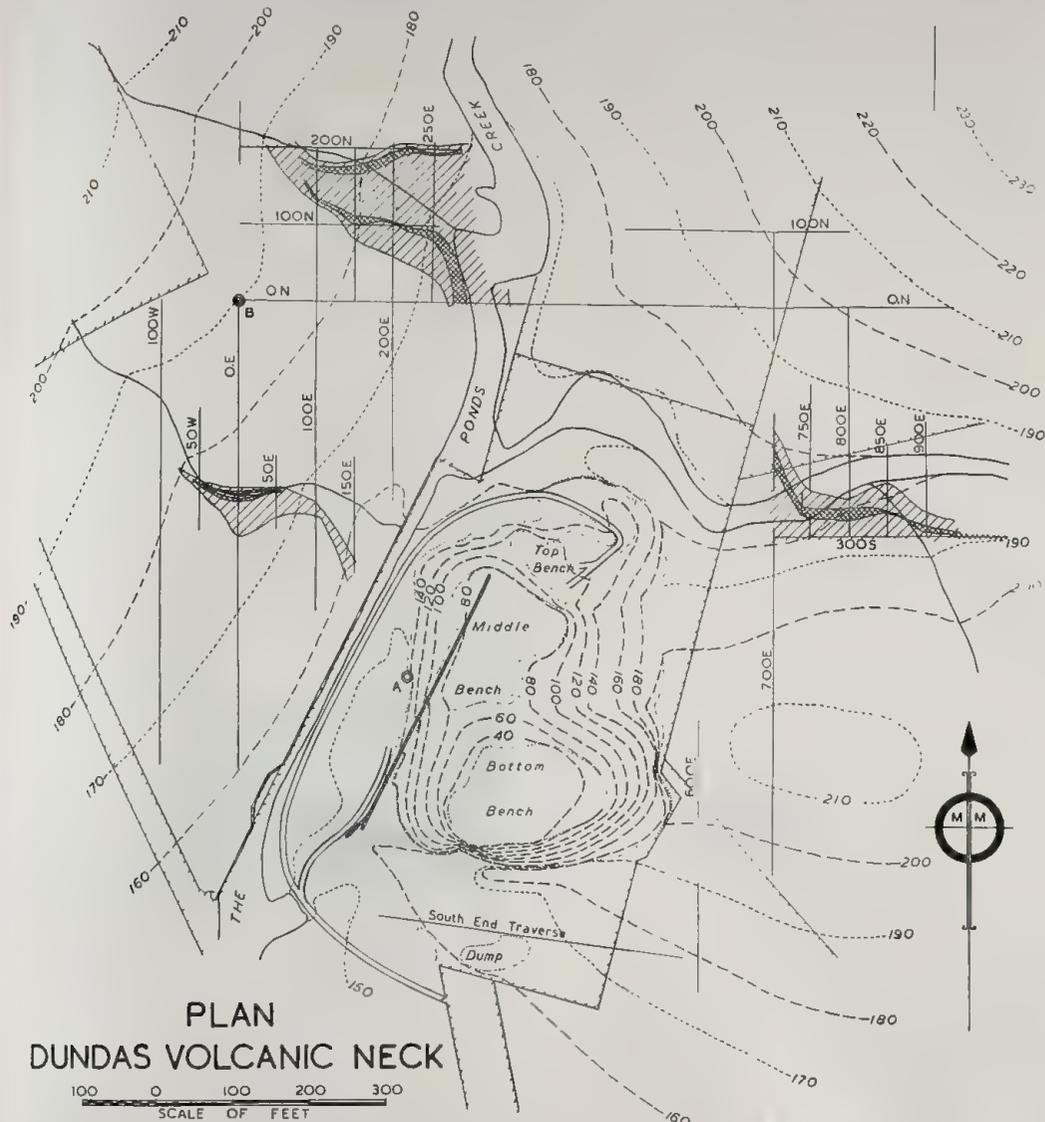
MAGNE



00W

100W





Surveyed 1940 Middle bench has since been extensively excavated almost to level of bottom bench

Datum for topographical survey A ⊙ Probable location of basalt dykes

Datum for magnetometric survey B ⊙ Areas which might possibly be underlain by basalt

Contours show approx. heights above sea level Contours every 20 feet thus — — — — — Alternate contours (Omitted in quarry)

Edges of quarry walls, bench floors & dumps Fences Magnetometer traverse lines

Roadways within boundaries of quarry lease Inclined tramway

Fig. 2.—Plan of Dundas Quarry.

H—May 7, 1947.

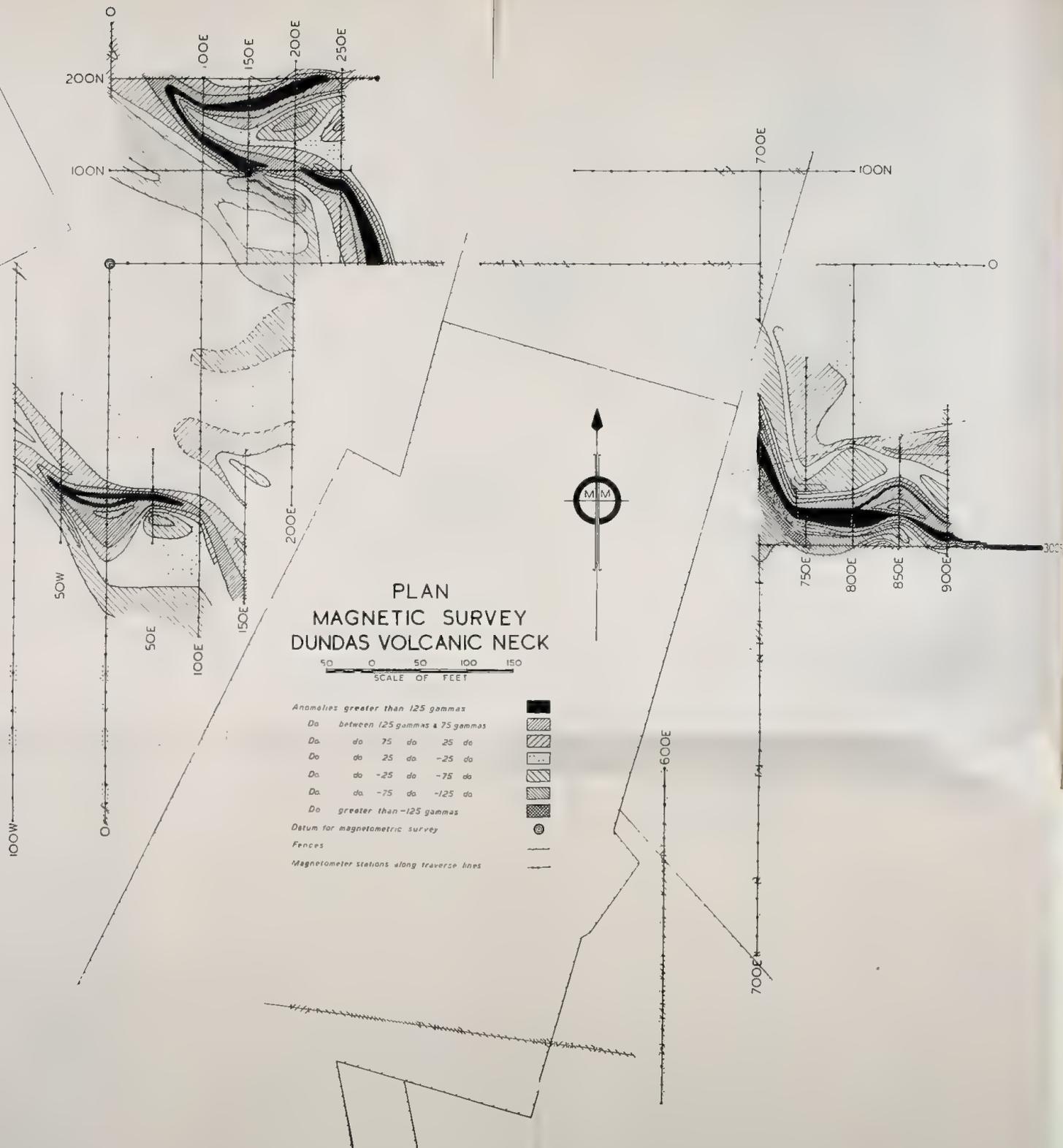
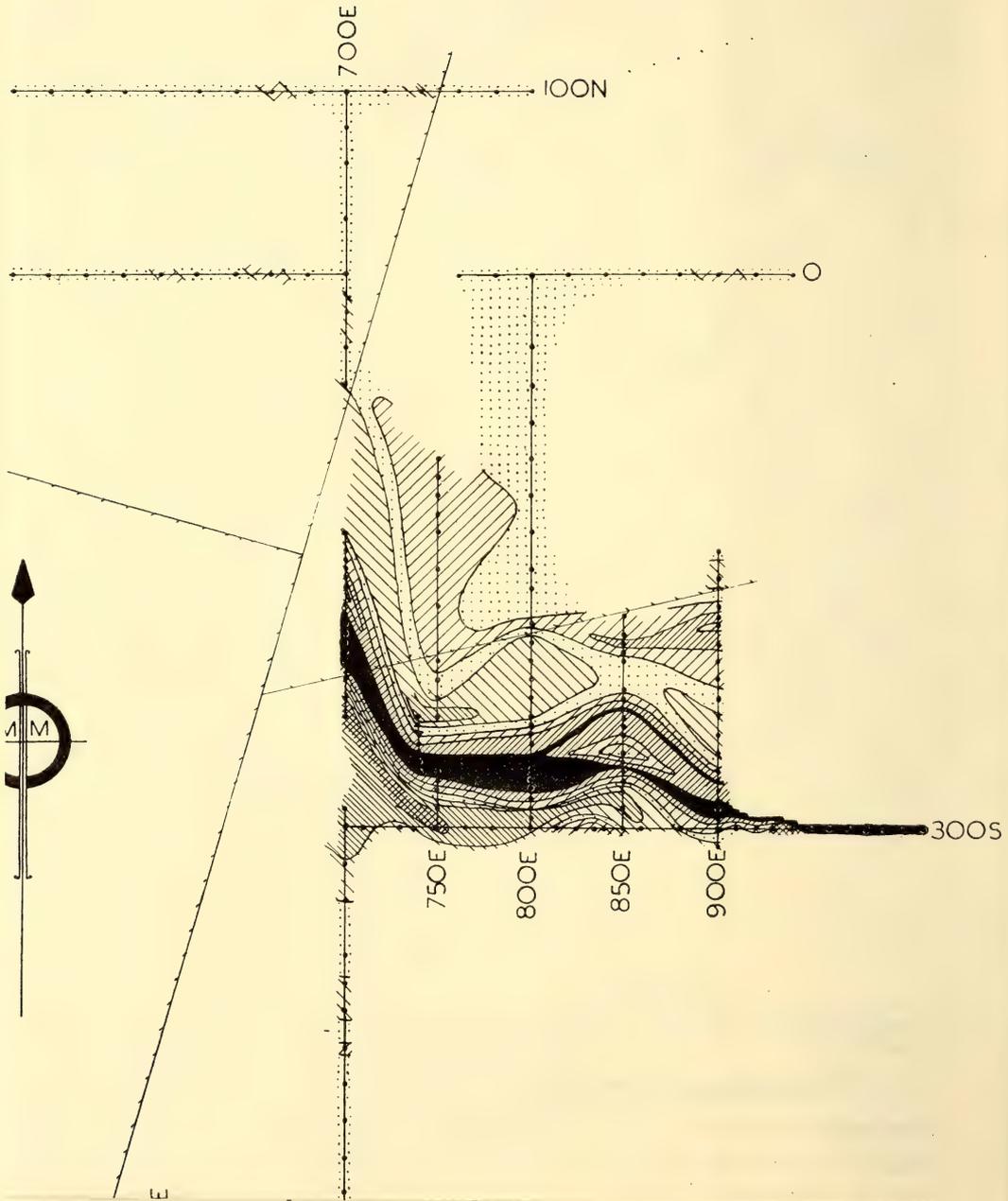


Fig. 3.—Plan of Magnetic Survey.



blackberry vines, which necessitated breaking the magnetometer traverses at these points. Photographs of some of the terrain over which the magnetometer traverses were made are shown on Plate II.

Magnetic Properties of the Rocks.

No direct determinations were made of the susceptibilities of the various rocks from Dundas. The following notes give probable figures for them.

Basalt.—The susceptibilities of specimens of basalt have been determined by several workers and figures ranging from approximately 500×10^{-6} to $10,000 \times 10^{-6}$ c.g.s. units have been quoted (Heiland, 1940). Samples of Tertiary basalt from Gulgong, N.S.W. (Booth and Rayner, 1933), had a susceptibility of approximately $5,000 \times 10^{-6}$ c.g.s. units. The susceptibility of the basalt from Dundas is probably of the same order.

Breccia.—Benson (1910) describes the breccia as consisting of fragments of shale, sandstone, quartzite, conglomerate, plutonic rocks and basalt. Its susceptibility is probably intermediate between those of the basalt and the sediments.

Shales and Sandstones.—The susceptibilities of these sedimentary rocks would be considerably lower than those of the basalt and breccia. Figures quoted by Heiland (1940) give values up to approximately 50×10^{-6} c.g.s. units for sedimentary rocks.

Results.

The results obtained are shown in Fig. 3. It will be seen that there are three main areas in which magnetic anomalies occur, one to the east of the northern end of the quarry, a second to the north-west and a third to the west of the quarry. In both of the former areas the positive anomaly has associated with it a negative anomaly of either comparable or somewhat smaller value. In the area to the west of the quarry the negative anomaly is either absent or not nearly so marked. The largest anomalies registered were +954 gammas at station 300S/950E and -623 gammas at station 300S/940E, but these were not typical. The largest anomalies on other traverses in the eastern area were ± 300 gammas. In the north-western area the largest anomalies were of the order of +200 gammas, while in the western area the largest anomaly was +175 gammas.

Along the traverse to the south of the quarry there were two points at which anomalies of -125 gammas occurred, but as one of these was adjacent to a wire fence and the other alongside an old dump, it was not considered that these were necessarily associated with masses of igneous rock. It was not possible to obtain a traverse line at this end of the quarry, which would be altogether free from such influences, owing to the presence of buildings, fences, dumps, etc.

The linear arrangement of the magnetic anomalies points to the igneous intrusions in the area being dykes. From their association with the volcanic neck they would obviously be basaltic in composition.

Three magnetic profiles (Figs. 4, 5 and 6) have been included to illustrate certain features of the anomalies. The main points of these profiles will now be described.

Profile O.E., Figure 4.—Along this traverse the readings obtained do not differ markedly from those at the base station O/O, except for the positive anomaly between 240S and 310S. It will be noticed that this anomaly may be due to the composite effect of three separate dykes. On traverses 50E and 50W these three peaks have coalesced to form one relatively narrow peak.

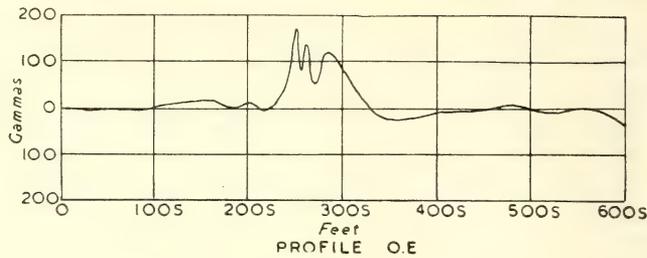


Fig. 4.

Profile 200E, Figure 5.—There are distinct negative anomalies showing on this profile. The first negative anomaly of 105 gammas is associated with a positive one of 160 gammas, while the second negative anomaly of 130 gammas is larger than the associated positive anomaly of 113 gammas. It can be seen from Fig. 3 that, further to the west, the positive anomalies join, one negative anomaly fades out, and the other becomes considerably reduced in magnitude.

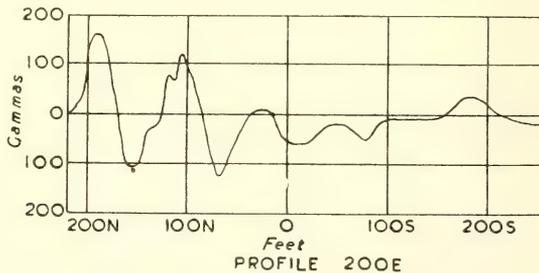


Fig. 5.

Profile O.N., Figure 6.—The only anomaly of any magnitude on this profile lies between 260E and 350E, and consists of a positive and associated negative anomaly. It again has the appearance of being a composite one due to the effect of two dykes, one being in such a position that its positive anomaly is masked by the negative anomaly of the other. The result is peaks of +170 and -12 gammas, with the corresponding negative troughs of -75 and -118 gammas respectively.

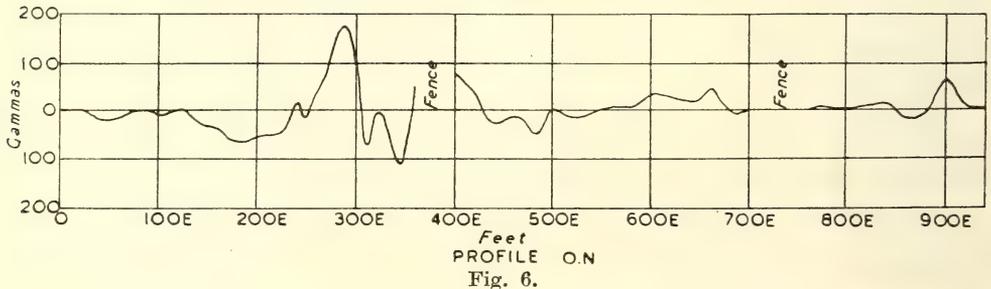


Fig. 6.

In cases where the negative anomaly is approximately equal to the positive anomaly, it is impossible to account for the shape of the magnetic profiles by assuming basalt dykes to be magnetized by induction in the earth's magnetic field only. It seems, therefore, in these cases, that either one face of each dyke possesses permanent south polarity or else the upper surfaces have irregular magnetic polarity. The splitting of the maximum vertical anomalies as shown on Fig. 3 could be due either to the splitting of the dykes which the anomalies represent or else to irregular polarity over the surface of a single dyke. The latter possibility implies a much greater total width of dyke and is considered to be a less likely explanation. Another possible, although perhaps an even less likely explanation, would be that the intrusive masses are more sill-like in character, of limited extent perpendicular to their length, and possess north polarity on one edge and south polarity on the other edge.

The relationship of the dykes to the neck is interesting. It is to be expected that the neck would have been located in an area where the volcanic products could most easily escape, possibly at the intersection of two sets of approximately vertical joints. The extent to which this original joint system might be modified due to strains set up by the intrusion and volcanic activity should be indicated by the disposition of dykes which might fill any fractures so formed. It is noteworthy that the dykes have been confined to three areas, with the possible exception of the area along the course of The Ponds Creek near the south-western corner of the quarry, where it was impossible to find suitable traverse lines. The western magnetic anomaly is approximately on the trend of a dyke which was exposed on the middle bench of the quarry at the time of the survey. Portion of the northern anomaly is also trending towards the neck. The eastern anomaly, on the other hand, does not show any evidence that it is radiating from the neck. The trends of individual dykes are irregular and the evidence is against the formation of any radiating series of fractures caused by the presence of the volcanic neck.

The relationship of the present drainage to the areas in which dykes occur has already been mentioned. This would hardly be so pronounced if the dykes had not originally outcropped. The outcrops have been obscured by weathering, but it is not considered that the weathering would be sufficiently deep or the dip of the dykes sufficiently low to necessitate any allowance being made for horizontal shift between the magnetic anomaly and the sub-outcrop, when calculating the position of the latter.

In order to delineate the probable location of the basalt dykes, as shown in Fig. 2, it has been assumed that there is a dyke, which is approximately vertical, associated with each appreciable positive anomaly. To allow for the possibility that the igneous masses are in the form of either dykes, with irregular surface polarity, or else sills as described above, areas in which an appreciable anomaly of either sign occurs have been classified as possibly underlain by basalt. These areas include those shown as the probable location of basalt dykes.

The only way to determine definitely which of the above assumptions is correct would be to prospect one of the areas by mining operations. In any prospecting outside the boundaries of the present quarry the magnetometric work has enabled the areas likely to be underlain by basalt to be confined to the three shown on Fig. 2. It is considered that the most likely spot for prospecting is the eastern area, because it was here that the anomalies were greatest. Of the two remaining areas the north-western seems the more favourable.

SUMMARY.

The volcanic neck at Dundas consists of a mass of breccia and basalt which has intruded Wianamatta shale. A magnetometric survey has shown that there are three areas adjacent to the neck which seem to have been intruded by igneous rocks. These intrusions are probably basalt dykes, which have weathered outcrops, and tend to split and follow irregular fractures in the country rock.

Plans of the neighbourhood of the quarry showing isogams and probable outcrops of the dykes, as well as examples of the magnetic profiles along some of the traverse lines, have been included.

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EXPLANATION OF PLATE II.

- Fig. 1.—The western face of the quarry, which is situated above and to the right of the inclined tramline, consists of a breccia composed of large masses of practically unaltered country rock, which has been brought up from the underlying sediments. On the extreme right of the photograph the face is composed of basalt. Portion of the floor of the top bench is showing in the foreground.
- Fig. 2.—View of the quarry looking north and showing the top and main portion of the middle bench. The latter has subsequently been further excavated and is now under water.
- Fig. 3.—View of south face of the quarry and portion of the floor of the bottom bench. The floor is now completely under water.
- Fig. 4.—View of the terrain to the west and north-west of the quarry. The base station for the magnetometer traverses is situated near the fence corner in the middle of the photograph. The western edge of the quarry is in the foreground. Just behind the quarry is the channel of The Ponds Creek. The area of the north-western magnetic anomaly is adjacent to this creek near the right-hand side of the photograph. The western anomaly occurs near the small tributary creek on the left of the photograph below the fence.
- Fig. 5.—View looking north-west. The area of the anomaly to the east of the northern end of the quarry is in the hollow in the centre and towards the right of the photograph.
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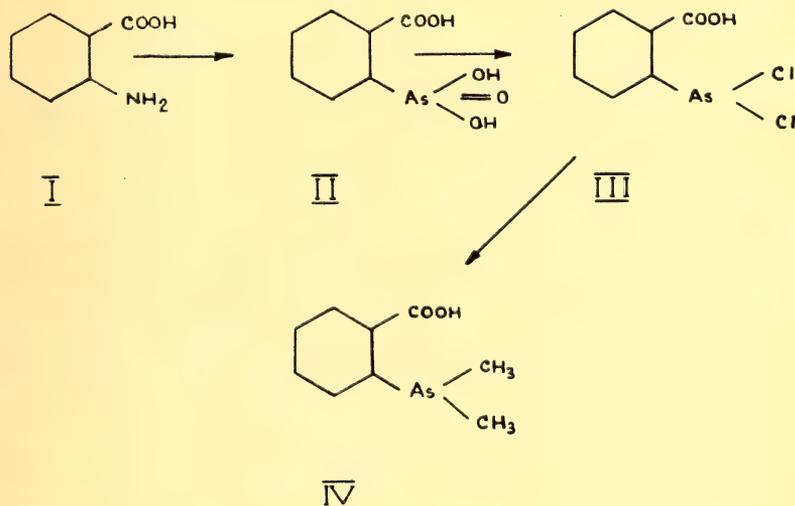
A NOTE ON THE PREPARATION OF SOME o-CARBOXY-PHENYL-ARSINE DERIVATIVES.

By G. A. BARCLAY, B.Sc.,
and R. S. NYHOLM, M.Sc.

Manuscript received, May 21, 1947. Read, June 4, 1947.

As part of a systematic study of the chelating properties of ortho substituted arsine derivatives, three carboxyl compounds have been prepared. Two of these (III and IV) have not been described previously, whilst the method employed for the other involved certain modifications to that used previously.

Starting from anthranilic acid (I), the following were prepared in succession: o-carboxy-phenylarsonic acid (II), o-carboxy-phenyl-dichlorarsine (III) and o-carboxy-phenyldimethylarsine (IV). The metal complexes of II and IV will be described in subsequent papers.



Anthranilic acid (I) was converted to o-carboxy-phenylarsonic acid (II) using the Bart reaction. Lewis and Cheetham (1923) used copper sulphate as a catalyst in this reaction, but did not describe the pure product. The preparation was carried out with, and without, the use of the catalyst, with no appreciable difference in yields. The pure compound was obtained as shining creamy plates, soluble in hot water.

The o-carboxy-phenylarsonic acid (II) was reduced to o-carboxy-phenyl-dichlorarsine (III) by sulphur dioxide in the presence of hydrochloric acid (Raiziss and Gavron, 1923*a*). The compound was obtained as white needle-shaped crystals, readily hydrolysed by water. Treatment of o-carboxy-phenyl-dichlorarsine (III) with methyl-magnesium iodide finally gave o-carboxy-phenyldimethylarsine (IV) as colourless, needle-shaped crystals, insoluble in water (Raiziss and Gavron, 1923*b*).

EXPERIMENTAL.

o-Carboxy-phenylarsonic Acid (II).

Anthranilic acid (92 g.) was finely ground and suspended in concentrated hydrochloric acid (200 ml.). This paste was cooled and diazotized in the usual manner with sodium nitrite (50 g.) in water (100 ml.). Some solid diazonium compound separated out but the whole suspension was added, with constant stirring, to a solution of arsenic trioxide (150 g.) and anhydrous sodium carbonate (310 g.) in water (1,000 ml.). The temperature rose from 30° C. to 40° C., a vigorous effervescence took place and the solution became a light orange colour. After stirring for half an hour, the solution was acidified with concentrated hydrochloric acid, filtered quickly, and allowed to stand overnight. Orange coloured crystals of the *o*-carboxy-phenylarsonic acid crystallized out, being obtained as shining creamy plates on recrystallization from water. Yield, 81 g. (49%). The compound did not melt below 360° C.; it was soluble in hot water, alcohol and sodium acetate solution, but insoluble in benzene and ether.

Found: C=34.02%, H=2.89%. Equivalent weight=123.7.

Calculated for $C_7H_7O_5As$: C=34.17%, H=2.87%; equivalent weight as a dibasic acid, 123.

o-Carboxy-phenyldichlorarsine (III).

o-Carboxy-phenylarsonic acid (50 g.) was dissolved in concentrated hydrochloric acid (500 ml.) and water (200 ml.). Sulphur dioxide was passed through this solution for fifteen hours at ordinary temperatures, the required compound being precipitated. Yield, 50.5 g. (94%). Recrystallization from toluene gave white needles melting at 156° C., which were insoluble in water but soluble in benzene and ether.

Found: C=31.52%, H=1.87%, Cl=26.3%.

Calculated for $C_7H_5O_2AsCl_2$: C=31.48%, H=1.89%, Cl=26.6%.

Note.—The melting point of this compound varies with the time of heating, only melting fairly sharply at 156° C. if placed in the bath at 150° C.

o-Carboxy-phenyldimethylarsine (IV).

o-Carboxy-phenyldichlorarsine (13.4 g.) in dry ether (50 ml.) was added gradually to a solution of methyl magnesium iodide prepared in the usual manner from methyl iodide (22.4 g.), magnesium (5 g.) and dry ether (100 ml.). The ether boiled vigorously and a yellow compound separated out, soon forming an oily, lower layer. The mixture was refluxed for one and a half hours and the complex was decomposed with water. After acidification with hydrochloric acid the required compound was extracted with ether. The *o*-carboxy-phenyldimethylarsine was removed from the ether layer by treatment with sodium carbonate solution and on treatment of the latter with hydrochloric acid the required compound was precipitated. Recrystallization from aqueous alcohol gave 8.1 g. (72%) of the compound melting at 133° C. The compound was insoluble in water but soluble in sodium acetate solution and in alcohol, benzene, ether and chloroform.

Found: C=47.64%, H=4.93%.

Calculated for $C_9H_{11}O_2As$: C=47.80%, H=4.90%.

SUMMARY.

The preparation of *o*-carboxy-phenyldichlorarsine and *o*-carboxy-phenyldimethylarsine from anthranilic acid are described. The use of a copper sulphate catalyst, in the Bart reaction used, was found to be unnecessary.

ACKNOWLEDGEMENT.

The authors wish to thank Miss J. E. Fildes for carbon and hydrogen analyses.

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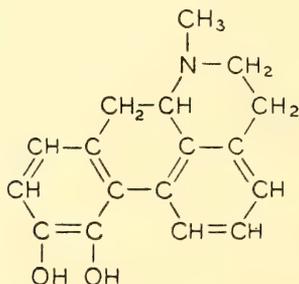
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THE COLORIMETRIC ESTIMATION OF APOMORPHINE.

By E. R. COLE, B.Sc.

Manuscript received, May 21, 1947. Read, June 4, 1947.

Apomorphine, a derivative of morphine, is obtained from the latter by heating under pressure with hydrochloric acid. It is sometimes used as an emetic, 1/10th grain producing vomiting within a few minutes. While processes for the estimation of apomorphine have been described, usually sufficient material is required to give about one grain of alkaloid (Glycart, 1926) and, as less than this quantity may be available, it seemed of interest to investigate the possibility of accurately estimating smaller amounts. Many sensitive reactions have been given for the detection of apomorphine but very few processes have been described for its colorimetric estimation. Walton and O'Brien (1931) described a process based on treatment with bromine. After addition of hydrogen peroxide to remove excess bromine, the solution is heated to bring about a colour change from red to green. The intensity of the final colour is proportional to the concentration of apomorphine. Palet (1918) used Gugliamelli's arsenotungstic and arsenotungstomolybdic reagents for the detection of apomorphine. These give a distinctive blue colour with the alkaloid and the reactions depend on the presence of phenolic hydroxyl groups in the molecule. Consideration of the structure of apomorphine shows that of the two phenolic groups present one has a free para position which is generally believed to be a primary requisite for condensation with a phenol reagent such as 2:6 dibromo-quinone chlorimide—Gibbs' reagent. The method to be described depends on this



APOMORPHINE

reaction in the presence of sodium bicarbonate, followed by extraction of the coloured product into butyl alcohol. The sodium bicarbonate serves to liberate the alkaloid from its salt and at the same time provides a slightly alkaline medium for the reaction. The procedure is simple and rapidly carried out and a distinct difference from the blank is noted with the lowest amount suggested in the range of standards.

EXPERIMENTAL.

(a) Reagents.

- (i) Solution of 2 : 6 dibromoquinone chlorimide, 23 mg. in 5 ml. absolute alcohol—freshly prepared. Gibbs' reagent.
- (ii) Sodium bicarbonate solution, 5% w/v freshly prepared.
- (iii) n-Butyl alcohol—reagent quality.
- (iv) Strong solution of apomorphine. 20 mg. of apomorphine hydrochloride dissolved in 10 ml. of distilled water containing 2-3 drops of hydrochloric acid (1 ml.=2 mg. apomorphine hydrochloride).
- (v) Dilute solution of apomorphine—prepared by diluting one part of strong solution to ten parts with distilled water. (1 ml.=0.2 mg. apomorphine hydrochloride.)

(b) Preparation of Standards.

In a series of stoppered test tubes—not more than half-inch diameter for convenient comparison later—place amounts of the dilute solution of apomorphine ranging from 0.1 ml. to 1.0 ml. with intervals of 0.1 ml. Dilute the smaller amounts to 1.0 ml. with the necessary amount of distilled water. Add *exactly* 0.1 ml. of Gibbs' reagent to each tube followed by 0.5 ml. of sodium bicarbonate solution. Mix well and allow to stand 30 minutes. Extract with 2 ml. of butyl alcohol by shaking vigorously. Allow the layers to separate completely for colour comparison.

A blank experiment on 1 ml. of distilled water should be included. For an estimation take 1 ml. of solution suitably diluted to bring the amount of apomorphine within the above range (0.02 to 0.2 mg.).

The final comparison of colour may be made as soon as the layers have completely separated, after about ten minutes standing.

DISCUSSION OF METHOD.

(a) *Colour of Butyl Alcohol Extract.* Gibbs' reagent gives a clear sky blue colour with phenol and with small amounts the intensity of colour is proportional to the concentration. With apomorphine and the procedure outlined, the colour of the butyl alcohol extract ranges from a slight greenish blue at first, through shades of purple to a bluish purple. Each step is well graduated and a distinctive range of colour is obtained which assists in the estimation of unknown solutions.

The introduction of the purplish shades appears due to further condensation of the blue derivative first formed with excess of the reagent, and for this reason it is necessary that exactly the same amount of reagent be added to each tube. The following experiment illustrates this point.

To several tubes containing 1 ml. of dilute solution of apomorphine were added respectively 1, 2, 3, 4, 5 and 6 drops of reagent, allowed to stand in the presence of sodium bicarbonate and completed as in method. The results are shown in the table.

Amount of Reagent Solution.	Appearance in Aqueous Phase.	Colour of Butyl Alcohol Extract.
1 drop	Clear blue.	Pale blue.
2 drops	Deeper blue with slight turbidity.	Gradually more intense colour of same shade.
3 „	Range of colour with increasing turbidity.	Off shade first appears—purple tint.
4 „		
5 „		
6 „		
	Turbidity masks true colour.	

Thus it will be seen that the off shades were introduced with the larger amounts of reagent.

A second experiment with the same amount of apomorphine and amounts of reagent from 4 to 9 drops confirmed this result. The introduction of the red shade continued with increasing excess of reagent.

(b) *Reagent Solution.* This should be freshly prepared as older solutions give a slight pink extract in the blank. While the lowest tube of the range is still distinguishable from the blank, it is obviously undesirable to introduce additional colour. It should be placed in a brown bottle during use.

(c) *pH of Reaction Medium.* It is interesting to note that the reaction takes place with reasonable speed in the presence of sodium bicarbonate, which gives a pH lower than that recommended for the condensation with phenol. Gibbs (1927) has found that the reaction velocity increases with increase in alkalinity and the rate of condensation with phenol starting with pH of 8.5 has been measured. Apomorphine, however, oxidizes rapidly in alkaline solution and it was considered desirable to reduce the alkalinity as much as possible. The time required for production of maximum colour in the presence of sodium bicarbonate is not unduly long and the result is obtained without interfering colour resulting from the decomposition of the reagent.

(d) *Time Required for the Reaction.* The optimum time was determined by allowing the reaction to proceed for different periods before extraction into butyl alcohol. Using 1 ml. of dilute solution of apomorphine it was found that 20-25 minutes were required for production of maximum colour and shorter periods showed marked difference in the colour extracted.

(e) *Extension of Range of Standards.* It is possible to extend the range to 1.6-1.8 ml. of dilute solution of apomorphine. Where more than 1.0 ml. is used it is advisable to increase the amount of butyl alcohol used for extraction to 5 ml. This reduces the intensity of colour and minimizes the loss of accuracy that otherwise results from the comparison of too deeply coloured solutions.

(f) *Interfering Substances.* It is clear that phenolic compounds which condense with the reagent will interfere with the determination.

APPLICATION TO HYPODERMIC TABLETS.

The tablets were labelled 1/10th grain apomorphine hydrochloride.

One tablet was dissolved in distilled water, 5 ml., containing one drop of hydrochloric acid. One ml. of this solution was diluted to 10 ml. and 1 ml. of the final solution used in the procedure described.

The resulting butyl alcohol extract was equivalent to that from 0.12 mg. of apomorphine hydrochloride (0.6 ml. of dilute solution), which indicates a content of 0.092 grain.

SUMMARY.

A method is described for the colorimetric estimation of apomorphine which depends on the condensation of the alkaloid with 2 : 6 dibromoquinone chlorimide in the presence of sodium bicarbonate and extraction of the coloured derivative into butyl alcohol.

The method has been applied to the assay of hypodermic tablets.

ACKNOWLEDGMENT.

The author wishes to thank the Government Analyst, Dr. H. B. Taylor, for permission to publish this paper.

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THEORETICAL ASPECTS OF THE MAXIMUM RECOVERY IN ABSORPTION OR STRIPPING OPERATION.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., M.Inst.Pet.

(Communicated by Dr. R. C. L. BOSWORTH).

Manuscript received, March 31, 1947. Read, June 4, 1947.

INTRODUCTION.

The amount of material that can be transferred from one phase to the other in a continuous counter current liquid-vapour extraction system is a maximum when the terminal conditions are in equilibrium. This generally calls for a system containing an infinite number of theoretical plates. This maximum transfer is taken as a basis for the computation of the efficiency of an absorption or stripping system.

Although it is comparatively easy to compute the magnitude of the maximum transfer when but one or two components may transfer from one phase to another, complications arise when the transfer of a multi-component material is under consideration.

Let us consider the general case of the absorption of a multi-component naphtha from the vapour phase by counter-current oil scrubbing with an incompletely stripped oil and equilibrium terminal conditions.

Under the assumed condition of equilibrium at the gas outlet the amount of component C_n absorbed will vary with the volume of oil. For small flows the effluent oil will be charged with component C_n to a state of equilibrium with respect to the entering gas; while, at the other end of the absorber, the emerging gas will not have attained a condition of equilibrium with the entering liquid on account of the limiting volume of the latter. As the oil flow is increased, the effluent oil will continue to be saturated while the condition at the gas outlet will approach equilibrium more closely so that more of component C_n will be recovered. Under the assumed conditions of complete interaction between the two streams there will come a stage at which equilibrium will be attained, with respect to C_n , simultaneously at both ends of the absorber, and under these conditions efficiency of recovery of C_n will attain a maximum.

Further increase in the oil flow beyond this stage will not improve the recovery because the effluent oil will no longer be saturated with respect to the incoming gas. There is consequently a critical oil flow giving equilibrium conditions at both ends of the system; increasing the oil supply beyond that amount would serve no useful purpose so far as recovery of C_n is concerned. However, the critical flow for C_n will, in general, not apply to any other component.

For any critical flow there will generally be only one component which will be present in both incoming and outgoing oils in equilibrium concentrations. Less volatile components will not saturate the rich oil but will be removed from the gas as completely as permitted by their original concentrations in the lean oil. Components more volatile than C_n will be incompletely removed from the gas because the oil will become saturated before the critical oil flow for these components has been reached.

For small transfers, as for example absorption from a lean gas with a high oil rate, the maximum transfer of each component may be calculated fairly accurately by applying the Sounders-Brown (1932) equation for the system containing an infinite number of theoretical plates. For large transfers, as for example absorption from rich gases with low oil rates, this method can lead to appreciable error due to large temperature and volume changes.

Up to the present there appears to have been no general method proposed for the calculation of this maximum transfer and it is the purpose of this paper to attempt to remedy this deficiency.

NOMENCLATURE.

The following nomenclature has been used in the derivation.

Without Subscripts.

L =the total mols of liquid phase entering the system in unit time.

V =the total mols of vapour phase entering the system in unit time.

With Subscripts.

C =the designation for a component.

K' =the equilibrium constant for a component under operating conditions at the top of the column, i.e. liquid entering.

K =the equilibrium constant for a component under operating conditions at the bottom of the system, i.e. liquid leaving.

L =the mols of liquid phase entering the system in unit time for the optimum transfer of a component, i.e. the critical flow for that component.

N =the mols of a component transferred from the vapour phase to the liquid phase in unit time. In stripping operation N is negative.

x =the mol fraction of a component in the liquid entering the system.

y =the mol fraction of a component in the gas entering the system.

Subscripts.

a for the least volatile of the naphtha components.

i for the general component when summing.

m for the most volatile of the naphtha components.

n for the general naphtha component.

$n-1$ for the naphtha component next less volatile than C_n .

p for any naphtha component less volatile than C_n .

$p-1$ for the naphtha component next less volatile than C_p .

q for any naphtha component more volatile than C_n .

$q-1$ for the naphtha component next less volatile than C_q .

DERIVATION.

For the purposes of the derivation the following assumptions have been made :

In unit time a total of V mols of raw gas containing $V \sum_{i=a}^m y_i$ mols of recoverable multi-component naphtha, is contacted with L mols of lean oil containing $L \sum_{i=a}^m x_i$ mols of the naphtha constituents, in an absorption tower operating under the following conditions :

- (1) The oil leaving and the gas entering the system are in equilibrium when there is sufficient of each naphtha component to saturate the oil with respect to the gas.

- (2) The oil entering the system has sufficient contact with the gas leaving the system to establish equilibrium where possible.
- (3) The vapour pressure of the naphtha-free oil entering the system is negligible under operating conditions. If this is not so the oil must be considered as an additional one or more components.

Conditions (1) and (2) normally require that the absorber contains an infinite number of theoretical plates.

Between the top and bottom of the absorption column there exists a pressure difference due to the resistance of the column packing or bubble plates to the gas flow, and a temperature difference due to the liberation of the latent heat of condensation of the absorbed naphtha. In the following calculation it is therefore necessary to use two equilibrium constants for each component, one for the conditions applying at the top of the column, and another for the conditions at the bottom of the column.

If the oil leaving the system has dissolved N_a mols of component C_a and N_n mols of component C_n , etc., by assuming Henry's law, if the effluent oil is in equilibrium with the incoming gas we can write

$$\frac{y_a}{K_a} = \frac{N_a + L.x_a}{L + \sum_{i=a}^m N_i} \dots\dots\dots (1)$$

and

$$\frac{y_n}{K_n} = \frac{N_n + L.x_n}{L + \sum_{i=a}^m N_i} \dots\dots\dots (2)$$

These equations express the condition of equilibrium with respect to components C_a and C_n respectively between the gas entering and the oil leaving the system. On the right-hand side the numerator represents the total number of mols of the component in the oil leaving the system in unit time, while the denominator represents the total number of mols of all kinds in the oil leaving in unit time.

Summing these for the whole of the naphtha gives (for equilibrium with the effluent oil)

$$\sum_{i=a}^m \frac{y_i}{K_i} = \frac{\sum_{i=a}^m N_i + L. \sum_{i=a}^m x_i}{L + \sum_{i=a}^m N_i} \dots\dots\dots (3)$$

Equation (3) can be rearranged in the form

$$\sum_{i=a}^m N_i = \frac{L \left(\sum_{i=a}^m x_i - \sum_{i=a}^m \frac{y_i}{K_i} \right)}{\sum_{i=a}^m \frac{y_i}{K_i} - 1} \dots\dots\dots (4)$$

Substituting (4) in (2) gives

$$N_n = \frac{y_n}{K_n} \cdot \frac{L \left(\sum_{i=a}^m x_i - 1 \right)}{\sum_{i=a}^m \frac{y_i}{K_i} - 1} - L.x_n \dots\dots\dots (5)$$

Inspection of equation (5) shows that N_n increases with L . However, there is an upper limit of L for which (1) and therefore (5) will hold because the maximum amount of component C_a that can be transferred from the gas to the

oil in unit time is limited to the difference between the amount entering with the raw gas and the amount leaving in the scrubbed gas which will be in equilibrium with the incoming oil. Therefore, increasing L beyond this critical value L_a will not further decrease the mol fraction of C_a in the gas.

Similarly, a critical value of L , L_n , will be found for the general component C_n beyond which an increase in L will not further decrease the mol fraction of C_n in the effluent gas. Once this stage has been reached for any component it is obvious that the optimum recovery has been obtained. However, a further small quantity will be recovered as the amount of effluent gas is reduced by the further absorption of the lighter components as L is increased. Once L has been increased beyond the critical value, L_n , for the general component C_n there will be insufficient of that component in the system to saturate the effluent oil with respect to the incoming gas.

Consequently equation (1) holds as long as the oil flow does not exceed that just required to give the optimum recovery of the least volatile component, C_a . Since equations (3), (4) and (5) are based on (1) they hold for values of L equal to or less than L_a . However, (2) holds as long as L does not exceed the critical value L_n .

Let us now consider the general case of the naphtha component C_n . As L is increased from $L_{(n-1)}$ to L_n components C_a to $C_{(n-1)}$ will be present in the effluent oil in insufficient quantity to be in equilibrium with the incoming gas, while components C_n to C_m will be present in equilibrium concentrations. Under these conditions (2) will hold but (1) will be invalid.

Summing (2) for components C_n to C_m gives, in parallel with (3) :

$$\sum_{i=n}^m \frac{y_i}{K_i} = \frac{\sum_{i=n}^m N_i + L \cdot \sum_{i=n}^m x_i}{L + \sum_{i=a}^m N_i} \dots\dots\dots (6)$$

whence

$$\sum_{i=n}^m N_i = \sum_{i=a}^m N_i \cdot \sum_{i=n}^m \frac{y_i}{K_i} + L \left(\sum_{i=n}^m \frac{y_i}{K_i} - \sum_{i=n}^m x_i \right) \dots\dots\dots (7)$$

For the naphtha components less volatile than C_n the amount absorbed is obtained from the equilibrium between the incoming oil and the effluent gas (assumption 2) as

$$N_a = V \cdot y_a - K'_a x_a \left(V - \sum_{i=a}^m N_i \right)$$

etc. to

$$N_{(n-1)} = V \cdot y_{(n-1)} - K'_{(n-1)} x_{(n-1)} \left(V - \sum_{i=a}^m N_i \right)$$

Summing these gives (for equilibrium with the incoming oil)

$$\sum_{i=a}^m N_i - \sum_{i=n}^m N_i = V \cdot \sum_{i=a}^{n-1} y_i - \left(V - \sum_{i=a}^m N_i \right) \cdot \sum_{i=a}^{n-1} (K'_i x_i) \dots\dots (8)$$

Substituting the value of $\sum_{i=n}^m N_i$ from (7) in (8) and rearranging gives the nett amount of naphtha transferred from one phase to the other in unit time for oil flow rates between $L_{(n-1)}$ and L_n as

$$\sum_{i=a}^m N_i = \frac{V \cdot \left(\sum_{i=a}^{n-1} y_i - \sum_{i=a}^{n-1} (K'_i x_i) \right) + L \cdot \left(\sum_{i=n}^m \frac{y_i}{K_i} - \sum_{i=n}^m x_i \right)}{1 - \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=n}^m \frac{y_i}{K_i}} \dots\dots\dots (9)$$

In the numerator on the right-hand side of this equation the coefficient of V is the fraction of the naphtha components less volatile than C_n recovered after allowing for losses in the gas leaving the system because of their presence in the incoming lean oil ; and the coefficient of L is the fraction of C_n and the more volatile components recovered after making the same allowances. The denominator is a factor correcting the result for the decrease in the amount of gas and the increase in the amount of oil brought about by the transfer of the naphtha from the vapour to the liquid phase.

Substituting this value of $\sum_{i=a}^m N_i$ in (2) and rearranging gives the transfer of C_n in mols per unit time as

$$N_n = \frac{y_n}{K_n} \frac{V \left(\sum_{i=a}^{n-1} y_i - \sum_{i=a}^{n-i} (K'_i x_i) \right) + L \left(\sum_{i=n}^m \frac{y_i}{K_i} - \sum_{i=n}^m x_i \right)}{1 - \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=n}^m \frac{y_i}{K_i}} + L \left(\frac{y_n}{K_n} - x_n \right) \dots \dots \dots (10)$$

Since the minimum concentration of C_n in the effluent gas is $K'_n x_n$ the actual amount thus leaving the system in unit time is given by

$$K'_n x_n \cdot \left(V - \sum_{i=a}^m N_i \right) = V \cdot y_n - N_n \dots \dots \dots (11)$$

If just sufficient oil has been passed to attain this condition (in which case $L=L_n$) the value of $\sum_{i=a}^m N_i$ given by (9) and the value of N_n given by (10) may be substituted in (11) to solve for L_n . This gives

$$L_n = \frac{V \left[\frac{y_n}{K_n} \left(K_n \left(1 - \sum_{i=n}^m \frac{y_i}{K_i} \right) - (K_n - 1) \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=a}^{n-1} y_i \right) - K'_n x_n \left(1 - \sum_{i=a}^{n-1} y_i - \sum_{i=n}^m \frac{y_i}{K_i} \right) \right]}{\frac{y_n}{K_n} \left(1 - \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=n}^m x_i \right) - x_n \left(1 - \sum_{i=a}^{n-1} (K'_i x_i) - K'_n \sum_{i=n}^m x_i + (K'_n - 1) \sum_{i=n}^m \frac{y_i}{K_i} \right)} \dots \dots \dots (12)$$

Now that the critical oil flow, L_n , has been determined we may proceed to estimate N_n and $\sum_{i=a}^m N_i$ for all conditions of oil flow.

For values of L less than L_n , N_n is given by (5) and (9) reduces to equation (4).

$$\sum_{i=a}^m N_i = L \cdot \frac{\sum_{i=a}^m \frac{y_i}{K_i} - \sum_{i=a}^m x_i}{1 - \sum_{i=a}^m \frac{y_i}{K_i}} \dots \dots \dots (4)$$

In this case the quantity recovered is independent of the gas flow and directly proportional to the oil flow.

For values of L between $L_{(p-1)}$ and L_p , L_p being equal to or less than L_n , $\sum_{i=a}^m N_i$ is given by (9), using the summation limits of $(p-1)$ and p in place of the

limits $(n-1)$ and n respectively. N_n is obtained by substitution of this appropriate value of $\sum_{i=a}^m N_i$ from (9) in (2) as

$$N_n = \frac{y_n}{K_n} \cdot \frac{V \left(\sum_{i=a}^{p-1} y_1 - \sum_{i=a}^{p-1} (K'_{i1} x_1) \right) + L \left(\sum_{i=p}^m \frac{y_1}{K_1} - \sum_{i=p}^m x_1 \right)}{1 - \sum_{i=a}^{p-1} (K'_{i1} x_1) - \sum_{i=p}^m \frac{y_1}{K_1}} + L \left(\frac{y_n}{K_n} - x_n \right) \dots \dots \dots (13)$$

In this equation the second function on the right-hand side gives the transfer of the component C_n without allowing for the change in the amounts of the two phases due to the naphtha transfer, and the first function is the correction for this effect.

For values of L between $L_{(q-1)}$ and L_q , where $L_{(q-1)}$ is equal to or greater than L_n , N_n is given by equation (11)

$$N_n = V \cdot y_n - K'_{n1} x_n \cdot \left(V - \sum_{i=a}^m N_i \right) \dots \dots \dots (11)$$

Substitution of the appropriate value of $\sum_{i=a}^m N_i$ from (9) then gives

$$N_n = V(y_n - K'_{n1} x_n) + K'_{n1} x_n \cdot \frac{V \left(\sum_{i=a}^{q-1} y_1 - \sum_{i=a}^{q-1} (K'_{i1} x_1) \right) + L \left(\sum_{i=q}^m \frac{y_1}{K_1} - \sum_{i=q}^m x_1 \right)}{1 - \sum_{i=a}^{q-1} (K'_{i1} x_1) - \sum_{i=q}^m \frac{y_1}{K_1}} \dots \dots \dots (14)$$

In this equation the first function on the right-hand side gives the transfer of component C_n without allowing for the change in the amounts of the two phases due to the naphtha transfer, and the second function is the correction for this effect.

This equation shows that, as discussed earlier, the recovery of C_n still increases slightly with the oil flow rates above the critical rate L_n . However, for values of L equal to or greater than L_m (14) reduces to

$$N_n = V \cdot y_n - V \cdot K'_{n1} x_n \cdot \frac{1 - \sum_{i=a}^m y_1}{1 - \sum_{i=a}^m (K'_{i1} x_1)} \dots \dots \dots (15)$$

and (9) reduces to

$$\sum_{i=a}^m N_i = V \cdot \frac{\sum_{i=a}^m y_1 - \sum_{i=a}^m (K'_{i1} x_1)}{1 - \sum_{i=a}^m (K'_{i1} x_1)} \dots \dots \dots (16)$$

Therefore, for oil flow rates greater than L_m the recovery of the total naphtha or any component is no longer increased by an increased oil flow.

The derivation above has been carried out without consideration of the direction of flow of the different components and may therefore be applied either to absorption (N_n positive and component C_n transferred from gas to liquid), or to stripping (N_n negative and component C_n transferred from liquid to gas). Indeed cases may arise in which both operations occur simultaneously in the one absorber. One particular component may undergo stripping while another undergoes absorption.

In the special case of scrubbing when the absorption oil has been completely stripped before entering the system, i.e. $x_n=0$ and $\sum_{i=a}^m x_1=0$, the critical oil flow from (12) simplifies to

$$L_n = V \cdot K_n \cdot \left(1 - \sum_{i=n}^m \frac{y_1}{K_1} - \frac{1}{K_n} \cdot \sum_{i=a}^{n-1} y_1 \right) \dots \dots \dots (17)$$

When the naphtha content of the gas is low, i.e. y is small, (17) approximates to

$$L_n = K_n \cdot V \dots \dots \dots (18)$$

This is the minimum value of L obtained from the Sounders-Brown (1932) equation for complete absorption with a perfectly stripped absorption oil in a column containing an infinite number of theoretical plates.

In the corresponding case for stripping when the incoming gas contains none of the naphtha (e.g. steam) $y_n=0$ and $\sum_{i=a}^m y_1=0$, and (12) simplifies to

$$L_n = \frac{K'_n \cdot V}{\left\{ 1 - \sum_{i=a}^{n-1} (K'_1 x_1) - K'_n \sum_{i=i=n}^m x_1 \right\}} \dots \dots \dots (19)$$

and when the naphtha content of the oil is low, i.e. x is small, (19) approximates to

$$L_n = K'_n \cdot V \dots \dots \dots (20)$$

This equation for stripping corresponds with (18) for absorption.

The bracketed functions in (17) and (19) give the quantitative effect in the change in composition of the oil and gas on the critical oil flow for the optimum (and in this case, maximum) transfer of C_n , for the simplified operation.

APPLICATION.

It must be remembered that the relationships and equations that have been derived in this paper are based on the assumption that terminal equilibrium conditions are obtained in the system and that under such conditions they accurately represent the naphtha transfer.

In practice equilibrium terminal conditions are never achieved as the rate of transfer of the naphtha from one phase to the other depends on the difference between the actual and equilibrium conditions. Therefore, for a condition of equilibrium to be achieved an infinitely large surface of contact between the two phases is required and this is equivalent to a negligible capacity for any apparatus of finite size. The approach to equilibrium in different systems varies and can, however, be exceedingly close at times. When only a small fraction of a component is absorbed the absorption is very close to the equilibrium value; the greatest deviation from the equilibrium absorption being with the component whose critical oil flow most closely approximates to the actual oil flow.

These points are perhaps best explained by an example. A slide rule was used for all calculations required.

EXAMPLE.

The following problem is discussed by Horton and Franklin (1940) in the calculation of absorber performance and design.

Absorber operating conditions.			
Operating pressure	4 Atm.	Absolute.	
Oil temperature entering ..	90° F.		
Oil temperature leaving ..	115° F.		
L =lean oil entering	1.00 mols per unit time.		
V =rich gas entering	0.9055 mol per unit time.		

Analyses. Mol Fractions.

	Rich Gas.	Lean Oil.
Methane	0.286	—
Ethane	0.157	—
Propane	0.240	—
n-Butane	0.169	0.02
n-Pentane	0.148	0.05
Absorption oil (non-volatile)	—	0.93

Since the absorption oil was not completely stripped, equation (12) is used to compute the critical oil flow for each of the components of the gas.

It is necessary to compute only sufficient of these values for two consecutive values to straddle the observed oil flow of $L=1.00$, but they have been calculated for all components for purposes of comparison. The intermediate stages of the calculation have also been included as their preparation greatly facilitates the calculations (Table 1).

Equilibrium constants used in the calculations were read from the nomograph of Scheibel and Jenny (1945, 1947). Since L is straddled by the critical value of the oil flow for propane and butane, the equilibrium transfer of methane, ethane and propane will be given by equation (13) and those of the n-butane and n-pentane by equation (14).

TABLE 1.

	Methane.	Ethane.	Propane.	n-Butane.	n-Peptane.	Oil.
y_n	0.286	0.157	0.240	0.169	0.148	—
$\sum_{i=a}^{n-1} y_i$	0.714	0.557	0.317	0.148	0	0
X_n	0	0	0	0.02	0.05	0.93
$\sum_{i=n}^m x_i$	0	0	0	0.02	0.07	1.00
K_m	53	9.8	3.1	1.15	0.37	0
$\frac{y_n}{K_n}$	0.0054	0.0160	0.0774	0.1470	0.400	—
$\sum_{i=n}^m \frac{y_i}{K_i}$	0.0054	0.0214	0.0988	0.2458	0.6458	—
K'_m	46	8.0	2.4	0.77	0.24	Nil
$K'_n X_n$	0	0	0	0.0154	0.01200	0
$\sum_{i=a}^{n-1} (K'_i x_i)$	0.0274	0.0274	0.0274	0.0120	0	0
L_n	47.2	8.20	2.26	0.6896	0.356	—
Equilibrium recovery, N_n	0.0076	0.0226	0.1098	0.1457	0.1281	—
Horton and Franklin recovery	0.0087	0.0178	0.1101	0.1407	0.1282	—

These equilibrium recoveries compare exceedingly well with those computed by Horton and Franklin by plate-to-plate calculations assuming four theoretical plates (Table 1). Actually their figures should be less than the equilibrium figures, but the assumptions necessary for their calculations could readily be responsible for this discrepancy.

From this example it can be seen that the computation of the equilibrium transfer by the method outlined in this paper can be of value in the calculations for absorber or stripper efficiency or design.

SUMMARY.

A general mathematical relationship based on Henry's law has been developed for the maximum transfer of (i) all components, (ii) any one component, of a multi-component mixture from one phase to the other in a counter current liquid-vapour system. Since the maximum transfer calls for equilibrium terminal conditions, the system must contain an infinite number of theoretical plates.

The derivation is based on the absorption of a multi-component "naphtha" from the vapour phase by counter-current scrubbing with an oil that has been incompletely stripped of the "naphtha" components before entering the system. The resultant equations apply to both absorption and stripping operation.

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THE OXIDATION POTENTIALS OF THE TRIS 1, 10
PHENANTHROLINE AND TRIS 2, 2' DIPYRIDYL
FERROUS IONS.

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Tris 2, 2' dipyridyl and tris 1, 10 phenanthroline (o-phenanthroline) ferrous salts are now widely used as redox indicators (Smith and Richter, 1944*b*). By the method of potentiometric titration Walden, Hammet and Chapman (1931, 1933) found the oxidation potentials of the tris 2, 2' dipyridyl and 1, 10 phenanthroline ferrous ions to have the same value, 1.14 volts, in molar sulphuric acid. Hume and Kolthoff (1943) repeated the determination for phenanthroline and obtained a value of 1.06 volts. They assumed that the dipyridyl potential was the same. Smith and Richter (1944*a*) found the dipyridyl potential to be different. In the latter work the potentials were determined as a function of acidity by two procedures: (i) simultaneous potentiometric titration of a mixture of simple ferrous and chelated ferrous ions with a suitable oxidant, and (ii) the ferrous complex was treated with sufficient oxidant to convert one-half to the ferric complex. The results were considered accurate to ± 0.02 volt.

In the present investigation the potentials have not been determined by titration procedures since there is evidence (Dwyer, McKenzie and Nyholm, 1944) that false equilibria may be involved; but instead the oxidized and reduced forms of the complexes have been isolated as the crystalline perchlorates, and then equimolar mixtures prepared in solutions of varying acidity and their potentials determined.

Both systems were found to be unstable owing to the tendency of the oxidized form to undergo reduction, and as a result it has not been possible to apply the Debye-Hückel limiting law for the estimation of the standard potentials.

The potentials were found to fall with increasing ionic strength as expected for a cationic system of this type. However, the stabilities of the two systems were found to be different with increasing acidity. As Smith and Richter (1944*a*) found, the dipyridyl complexes became highly unstable above normal acid concentration. On the other hand the phenanthroline complexes were least stable in weakly acid solution. Since the effect of acid is to form a salt with the basic chelating group, and hence decompose the complex, the behaviour of the dipyridyl complexes is to be expected. The behaviour of phenanthroline is similar to that of the ruthenium compounds (Dwyer, Humpoletz and Nyholm, 1946) and the same explanation, as was put forward in that case, probably also applies, i.e. at the high potentials which occur in the weakly acid solutions the 1, 10 phenanthroline itself is oxidized to 2, 2' dipyridyl 3, 3' dicarboxylic acid.

As a result of these opposite stabilities in acid solution it has not been possible to compare accurately the potentials of the two systems over the whole range of acid concentrations, but in the limited range where a comparison was practicable the phenanthroline potential was usually 28mv. higher.

The dipyridyl ferrous ion is obviously not as satisfactory redox indicator in mineral acid solution as the phenanthroline ferrous ion.

EXPERIMENTAL.

Tris 1, 10 phenanthroline ferrous perchlorate.

Ferrous ammonium sulphate (0.4 g.—1 mol.) was dissolved in cold water (20 mls.), and 1, 10 phenanthroline (0.65 g.—3.1 mols.) stirred in, until completely dissolved. The deep red solution was filtered, heated to 60° C. and perchloric acid (60 per cent.) added drop by drop with vigorous stirring to induce crystallisation. The deep red crystals obtained on cooling were washed with dilute ice-cold perchloric acid and finally with ice water. The substance was dried over concentrated sulphuric acid.

Tris 1, 10 phenanthroline ferric perchlorate.

The tris 1, 10 phenanthroline ferrous sulphate complex was prepared as before, cooled in ice and saturated with chlorine until the colour changed to blue. The mixture was then heated to 40° C. and perchloric acid added as before. The deep blue crystals obtained by cooling in ice were washed with dilute ice cold perchloric acid containing a little chlorine, and finally with ice-cold chlorine water. The filtration was carried out in sintered glass to avoid reduction by filter paper. The substance was finally dried over calcium chloride in an atmosphere of chlorine.

Dipyridyl Compounds.

These were prepared as above, except that the solutions were kept twice as concentrated to compensate for the much greater solubility of the complexes. In appearance the compounds were similar to the phenanthroline compounds; the ferric compound, however, was light blue with a slight green tint.

TABLE I.

Formulae.	Mol. Wt.	Per Cent.			
		N.		Fe.	
		Calc.	Found.	Calc.	Found.
$(C_{12}H_8N_2)_3Fe(110_4)_2 \cdot 4H_2O$	867.5	9.69	9.62	—	—
$(C_{12}H_8N_2)_3Fe(ClO_4)_3 \cdot 6H_2O$	1003.0	8.38	8.38	5.57	5.7
$(C_{10}H_8N_2)_3Fe(ClO_4)_2 \cdot 4H_2O$	795.4	10.57	10.68	—	—
$(C_{10}H_8N_2)_3Fe(ClO_4)_3 \cdot 6H_2O$	931.0	9.03	9.03	6.00	6.02

Redox Potentials.

The redox vessel and electrical apparatus were similar to that described in a previous communication (Dwyer, McKenzie and Nyholm, 1944). The potential of the saturated colomel half cell was taken as 0.2442 volts 25° C.

Sufficient of the ferrous and ferric complexes to prepare 50 mls. of 0.0005 M solution of each was weighed in individual small tubes. The ferrous salt was then quantitatively transferred to 40 mls. of sulphuric acid of the appropriate concentration in the redox vessel, traces of residual material being washed in with a further 5 ml. of acid. The material was dissolved as rapidly as possible in a current of purified nitrogen and the ferric salt then added as above. This order of solution tends to stabilize the ferrous/ferric ratio. The potential was determined immediately and at suitable intervals thereafter. With the phenanthroline complexes in solutions of high acidity (5 to 7 N.) the potential rose about 2 mv. in the first ten minutes then fell slowly, until at the end of an hour it had fallen about 5 mv. This was due to decomposition of the ferric

complex as the solution finally changed from purple to red overnight. In the lower acid ranges the potential commenced to fall from the initial value, the rate increasing with decreasing acidity. In the mixture containing no added acid the rate of fall was 2 mv./min. over the first twenty minutes, becoming even greater as time proceeded. The highest potential was accepted as the redox potential. The measurements, which are summarized in Table 2 and Fig. 1, are considered accurate to ± 2 mv., except in the very dilute acid solutions (0.1 N or less), where the accuracy is probably ± 5 mv.

TABLE 2.

Normality of Acid.	Potential in Volts.			
	Authors' Values.		Smith and Richter Values.	
	Phenanthroline.	Dipyridyl.	Phenanthroline.	Dipyridyl.
None added ..	1.120	1.096	—	—
0.01	1.112	1.084	—	—
0.103	1.102	1.071	—	—
0.5	1.086	—	—	—
1	1.073	—	—	—
2	1.057	—	1.06	0.97
4	1.028*	—	1.03	—
5	1.015	—	—	—
6	0.996*	—	1.00	—
7	0.977	—	—	—
8	—	—	0.96	0.92

* From Fig. 1.

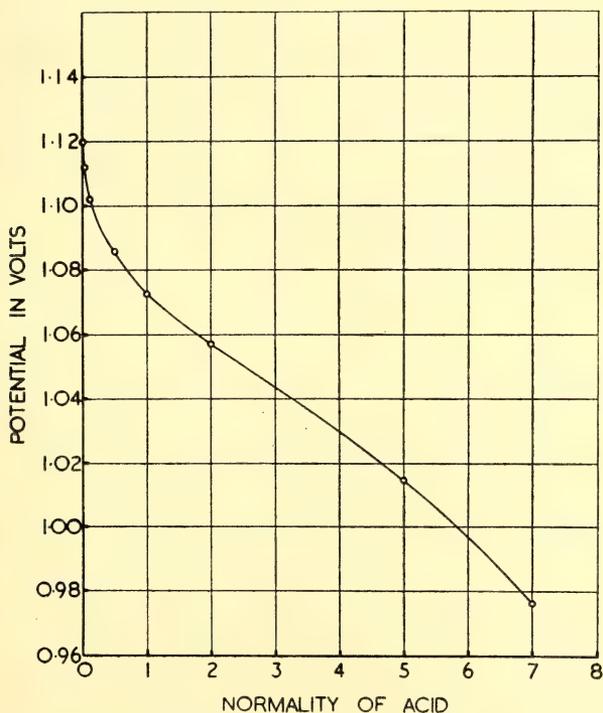


Fig. 1

The potential of the dipyriddy complexes could not be determined satisfactorily above an average concentration of 0.1 N. Even at this acid concentration, the potential fell at the rate of 0.5 mv./min. In the acid concentration of normal and higher it was impossible to obtain a potential value owing to the rapid fall. These solutions became quite colourless overnight, but the red ferrous complex could be regenerated by the addition of alkali.

Attempts were also made to determine the dipyriddy potentials in hydrochloric and nitric acid solutions. While the complexes were somewhat more stable in these acids, the improvement was not sufficient to obtain an accurate measure of the potentials at the higher acidities.

The values obtained for dipyriddy are shown in Table 2.

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SUMMARY.

The redox potentials of the tris 1, 10 phenanthroline and tris 2, 2' dipyriddy ferrous ions have been determined by the standard method of dissolving pure specimens of the oxidized and reduced forms in solutions of varying acid concentration. In 0.103 N sulphuric acid the potentials are 1.102 and 1.071 volts respectively.

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A NOTE ON THE INSTABILITY CONSTANT OF THE TRIS 2, 2' DIPYRIDYL FERROUS ION.

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The instability constant of the tris o-phenanthroline (1, 10 phenanthroline) ferrous ion has been determined by Dwyer and Nyholm (1946) by a redox method, which depended essentially on the observation that ferric iron does not react directly with phenanthroline. The potential of an inert electrode in an acid mixture of ferrous and ferric ions was measured before and after the addition of a known amount of phenanthroline. From the data for the phenanthroline complex and the oxidation potentials of the tris 1, 10 phenanthroline and tris 2, 2' dipyridyl ferrous ions obtained by Smith and Richter (1944), an estimated value of the instability constant of the tris 2, 2' dipyridyl ferrous ion of 1×10^{-15} was obtained. In the present note a direct determination of the instability constant of the tris 2, 2' dipyridyl ferrous ion is described.

In the previous paper it was shown that the instability constant K_I could be derived from the equation

$$K_I = 10^{-\frac{\Delta E}{0.059}} \times C_B^3$$

Where C_B is the concentration of free chelating group and $\Delta E = E_2 - E_1$, E_1 being the potential of the ferrous-ferric couple before the addition of the chelate and E_2 the final equilibrium potential after addition. In the acid solutions employed the chelate is largely present as the ion BH^+ and the concentration of free bases can be obtained from the hydrolysis constant K_H , whence

$$K_I = 10^{-\frac{\Delta E}{0.059}} \times \left[\frac{K_H \times C_{BH^+}}{C_{H^+}} \right]^3$$

EXPERIMENTAL.

Hydrolysis Constant of 2, 2 Dipyridyl.

Dipyridyl 0.025 g. was dissolved in sulphuric acid (5 mls., 0.1 N) and diluted to 100 mls. with distilled water. The pH, as found with the glass electrode, was 4.74. Making similar assumptions as in the previous paper the hydrolysis constant

$$K_H = 10^{-4.4}, \text{ or } pK_b = 9.6 \text{ at } 25^\circ \text{C.}$$

Albert and Phillips (1946) by a potentiometric method reported $pK_b = 9.77$ at 20°C .

The instability constant of the tris 2, 2' dipyridyl ferrous ion.

One millilitre each of 0.1 M ferrous ammonium sulphate and ferric ammonium sulphate (0.5 N and 0.25 N with respect to sulphuric acid respectively) were mixed and made up to 100 ml. with dilute sulphuric acid. The concentration of sulphuric acid used was such that the pH of the mixture lay between 1.37 and 2.3 over the four determinations. The pH and redox potential were then determined, and a known weight of 2, 2' dipyridyl added, the weight being in excess of that necessary to form the ferrous complex but insufficient to raise the pH to the point of

precipitation of ferric hydroxide. The mixture was thoroughly stirred and the redox potential and pH determined at suitable intervals until equilibrium was attained. This usually took about an hour. The results are summarized in Table 1. In calculating the mean value and

TABLE 1.

Experiment No.	Initial pH.	Initial Redox. (Volts.)	Wt. of Dipyridyl (Gms.)	Final pH.	Final Redox. (Volts.)	E. (Volts.)	Conc. BH. + (moles/litre).	pK ₁ .
1	2.30	0.450	0.15	2.71	0.667	0.217	0.0066	15.3
2	1.94	0.446	0.1	2.05	0.574	0.148	0.00346	16.9
3	1.37	0.442	0.1	1.56	0.525	0.083	0.00346	17.2
4	1.98	0.446	0.2	2.20	0.666	0.220	0.0098	16.3

standard error of the instability constant the logarithmic transformation has been made, giving a value of $10^{-16.4 \pm 0.4}$. This instability constant is significantly larger than that of the 1, 10 phenanthroline complex ($10^{-17.7 \pm 0.5}$) and is in accord with the observation that the dipyridyl complex is less stable than the phenanthroline complex. The error in the estimated value for dipyridyl (10^{-16}) lies in the difference in hydrolysis constant of the chelates and an error in Smith and Richter's value of the oxidation potential of the tris 2, 2' dipyridyl ferrous ion (Dwyer and McKenzie, 1947).

SUMMARY.

The instability constant of the tris 2, 2' dipyridyl ferrous ion has been determined by a redox method and found to be $10^{-16.4 \pm 0.4}$.

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POSSIBLE CAUSES OF INTRAFORMATIONAL DISTURBANCES IN THE CARBONIFEROUS VARVE ROCKS OF AUSTRALIA.

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With Plates III-IV.

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I. INTRODUCTION.

Australia possesses some of the most interesting varve rocks in the world. In Carboniferous and Permian times in New South Wales there were at least six glacial stages, and particularly in the peri-glacial lakes of Middle Carboniferous (Kuttung) times there were laid down clays with beautifully distinct seasonal banding. Today these beds are found in a scarcely altered condition, regionally tilted and somewhat folded in places, but for the most part totally unmetamorphosed. In them are bands of remarkable intraformational folds and other disturbances of penecontemporaneous nature, which have long puzzled geologists. No universally accepted explanation has yet been proposed for them.

The best known intraformational contortions in varve rocks are found in the Hunter River Valley of New South Wales, where they were first reported by Sussmilch and David (1919). Others have described them from many parts of New South Wales. They are also known in South Australia. Mawson (1926) noted that the conditions for the formation of varved clays would be found in lakes occupying "over-deepened, rock-bound basins or produced by moraine dams or ice blockages". Such conditions, he observed, were rare during the Permo-Carboniferous in South Australia, but nevertheless, some small examples have been found and in them are contorted layers, e.g. near Normanville, S.A., where there is puckering over a six-inch layer.

Similar contortions are not restricted to varved clays, but often occur in other glacial rocks of Carboniferous and Permian times, such as the glacio-fluvial and glacio-lacustrine sandstones and silts of Victoria, South Australia and Western Australia. More attention, however, has always been paid the disturbances in varved rocks, because of the striking lamination and often perfect preservation of the small structures.

Varve rocks are also believed to be associated with the late pre-Cambrian glaciation in Australia. The Tapley's Hill slates of the Adelaide series of South Australia have often been described as varved deposits, but are now recognized as not actually varved, although strikingly laminated. Their non-varved nature is clear under the microscope. They do not show contemporaneous contortions at their type locality near Adelaide. The regular flexures at Tapley's Hill Quarry and elsewhere appear to me to be tectonic, though the rocks admittedly must have been folded while still very plastic. From another locality, however, apparently also of late pre-Cambrian rocks (Mawson's Torrowangee series) at Campbell's Creek, near Poolamacca, north of Broken Hill, N.S.W., Andrews and Browne collected an example of contemporaneously contorted varved shale, which David (1922) exhibited alongside Seaham samples to the 1st Pan-Pacific Science Congress, at Honolulu in 1920. Intraformational disturbances are also known in many other horizons of the Adelaide series (Howchin, 1920), a fact which I have recently been able to confirm at many points in the Mt. Lofty and Flinders Ranges.

The object of this paper has been to discuss Australia's best-known contorted glacial beds, in the varves of the Hunter River area, and, bearing in mind evidence of other examples, to attempt an explanation of general validity for this type of intraformational contortion.

II. THE NATURE OF THE DISTURBANCES.

1. Discovery of the Carboniferous Varves in the Hunter Valley.

The discovery by David of tillite in the Kutting series of the Hunter River Valley on the British Association excursion in company with Penck and Coleman on 22nd August, 1914, led to the discovery of widespread glacial remains of Carboniferous age in this area. Permian glacials of course had been known here since the days of Oldham. In 1919 Sussmilch reported the presence of varved rocks here; he had no hesitation in interpreting them, as in North America and Europe, as the result of alternating seasonal deposition of glacial material in a lake. No one doubts this interpretation in view of their typical "varve" structure, their association with striated boulders in the adjacent tillites, and remembering the striated pavements of unquestionably glacial origin at Wolfingham, only nine miles N.W. of Maitland, New South Wales (Osborne and Browne, 1921). In the other States similar relationships are known in the Permian, as at Hallett's Cove and Inman Valley, South Australia, and at Bacchus Marsh, Victoria.

Referring to Sussmilch and David (1919) on the Hunter River Valley exposures, we read: "At intervals in the varve shales there occur layers which

are strongly contorted, similar to those described by Sayles from the Squantum Beds. These contorted layers range from a few inches up to four feet in thickness, and display in miniature every type of Alpine folding . . ." (see their plates XXIV, XXVI and XXVII). "A bed which is contorted in one part may fade out into a part which shows no contortion at all, while the contorted layers themselves are interstratified between perfectly regular unfolded layers. The whole evidence suggests that the contortion is contemporaneous . . ."

2. Opinions on the Structures at Seaham.

So far, so good, but what of the cause of these contemporaneous contortions? Sussmilch suggests that they are "due to the stranding of floating masses of ice, or perhaps in some cases to the temporary forward movement of the ice front" (*loc. cit.*, pp. 272, 273). David (1922) suggests "the movement of ice in some form tending to develop horizontal gliding planes". It is very interesting to note (in Sussmilch, *loc. cit.*) that "delicate, but well-preserved annelid tracks are found in the bedding planes of some of the varve shales", proving that the beds are water-laid, and thus cannot be dismissed as "englacial melts" (see Carruthers, below). A similar case of contorted structures in varves containing arthropod tracks is known in the European Pleistocene (Schwarzbach, 1938).

In the following years Osborne carried out an extensive survey of that part of the Hunter Valley area where these glacial lake beds are best exposed, especially around the abandoned town site of Seaham (1922*a* and *b*; 1925*a* and *b*; 1927). Without making a special study of varve contortions, he followed in general the opinions of David and of Sussmilch. Osborne made a notable contribution, however, in pointing out that "peculiar relationships between some of the varve rocks and either sandy or tuffaceous rocks are to be found in many parts of the area" (1925*a*, p. 75). With great kindness he has personally shown me sections illustrating this "intimate co-mingling of the two units, shale and tuff or sandy sediment. At times there is a suggestion that the tuffaceous material has been injected into the varve rock, while at other times the reverse seems to be indicated." Rightly, I think he rejected any idea of intrusion, recognizing the disturbance as contemporaneous, and gave two alternative suggestions:

- (a) "The structures may possibly be explained by considering the effect of differential movement (gliding) upon a series of partially consolidated sediments" (1922*a*, p. 183).
- (b) "Other structures . . . seem . . . to have been produced as a result of the dragging force of moving ice . . . Layers of twisted varve rock pass into breccia bands, followed by more shale, and finally massive tuff."

Evidently the two had been laid down normally in succession, some of the tuff hardening more quickly than the varve clay, which one would expect would keep its plasticity for some time. At this stage, he concluded, a movement of ice interfered, producing shattering, injection and foliation. Contemporaneous erosion and current scour were also noted in the varves.

In 1935, for the Melbourne A.N.Z.A.A.S. meeting, Sussmilch restated his opinions on the cause of the varve contortions as follows: "Such folding is contemporaneous, and must have taken place while the varve layers were still soft, and must have been caused by ice movement of some kind, possibly the dragging movement of stranded masses of floating ice along the lake bottom. It has been suggested that it might have been caused by the "slumping" of layers of inclined sediment, but the whole of the evidence indicates that the varves now contorted were deposited as practically horizontal layers, consequently gravity could not have come into operation." There is a big difference,

however, between apparently or "practically horizontal", as we shall see in Part III, Section 7, where it is suggested that in fact slumping may occur on slopes so gentle that they could not normally be detected by the eye.

The Swedish geologist Caldenius, from de Geer's Institute for Glacial Chronology in Stockholm, visited Seaham later and made a special study of the varves (1938). Recognizing the contemporaneity of the contortions with the sedimentation, he gives two explanations, the disturbances being due, he says,

- (a) to "small slidings during the time of the existence of the lake", or
- (b) to "the readvance of the land-ice".

The ribboned structure with thickening and thinning suggested slides to him (p. 362). Most of the contortions, he says, originated from settling of some part or other of the lake bottom. They might also be formed when "pebbles and blocks from drift ice had fallen down to the bottom or when icebergs, weighed down by their moraine burden, had sunk" (p. 361). In this case, we may note, an intercalation of tillite should be found adjacent to the disturbed beds, and such is the case in one place (see p. 358). Caldenius also remarks that even where the varves appear to be of a more distal nature (in relationship to the source of material at the snout of the glacier), contortions still occur.

The roadsides and quarry at Seaham rapidly became a geological "classic" after their initial discovery, so that David took steps to have the quarry in particular preserved as a cultural monument. Osborne recounted to me how, at the Pan-Pacific Science Congress excursion here in 1923, the assembled scientists clambered all over the quarry, rediscovering in miniature all the tectonic structures they knew so well from the Alps. This analogy with Alpine tectonics serves to illustrate my own interpretation, as we shall see in due course.

3. Other Examples.

Elsewhere in the Hunter River valley area it is the same. For example, Carey (1937) describes how, at the gap west of Werrie Creek, "the varves are 250 feet in thickness, and towards the top there is a sudden disposition to contortions, yielding some beautiful specimens, due to the impress of over-riding glaciers of an advancing ice-sheet" (p. 365). They are overlain by tillite which may be taken as representing a glacial readvance; so his interpretation is apparently supported by this. On the other hand, at another place, his "Landslide Section", we read how in a three hundred-foot section of varves the contortions occur in the lower parts (p. 347). In this case they are not immediately overlain by tillite, as one would expect if they had been due to a glacial readvance.

The same appears to be true in the Gosforth district, where Browne found good examples of contorted varves at certain well-marked horizons (1926, p. 242); his best section was one-quarter of a mile west of Mr. B. Cant's house. Another good locality is Browne's Creek near Currabubula (15 miles west of Tamworth), where Benson (1920) found a section of varves overlain by mudstones. He sketches a typical example of contorted varves in his fig. 4 (p. 298); in his fig. 5 he shows a rounded granite boulder, which not only bends down the underlying varves, but minutely crumples them *on one side only* in the manner of exotic blocks in the Alpine "Wildflysch", where gravity sliding is generally called in to account for the distribution of large boulders rather than the agency of floating ice. Angular granite blocks are shown in Benson's fig. 6. It is not suggested, of course, that floating ice is out of the question here; quite the contrary, but it is perhaps well to consider other possibilities.

Looking farther afield, in rocks more of Permian than of Carboniferous age, to Victoria, South Australia and Western Australia, we note that varve shales are

rarer (see Mawson's example, noted above), though intraformational contortions are common enough in the glacio-lacustrine sandy formations, e.g. in glacio-lacustrine sandstones in the lower quarry at Bald Hill, two miles N.W. of Bacchus Marsh, Victoria (Summers, 1923, notes how the "peculiar crumpling in the sandstones has been ascribed to the action of stranding ice"); again, in the River Finniss glacial sandstones of South Australia (Howchin, 1910, illustrates them and explains them as "produced by the ploughing movement of ice-masses"); in Western Australia, in the glacial sandstones of the Lyons series of the North West Basin (Raggatt, 1936, speaks of "the pushing action of grounding ice rafts"). Some of the Finke River, S.A., contortions appear to be similar (David and Howchin, 1923).

4. Types of Structures Involved.

My own impression of the intraformational contortions in the varves at Seaham and elsewhere is that there are four principal types of structure:

- (a) Large overfolds, sometimes grading into overthrusts or "nappes", involving up to ten or more individual annual varve layers, and ranging in amplitude up to 3-4 feet high (see Fig. 1, and Plate III). They rest on normal flat-lying beds and are in turn overlain by flat-lying beds. The contact with the latter is an erosion plane. The direction of the overfolding is generally the same in any one outcrop, but I was not able

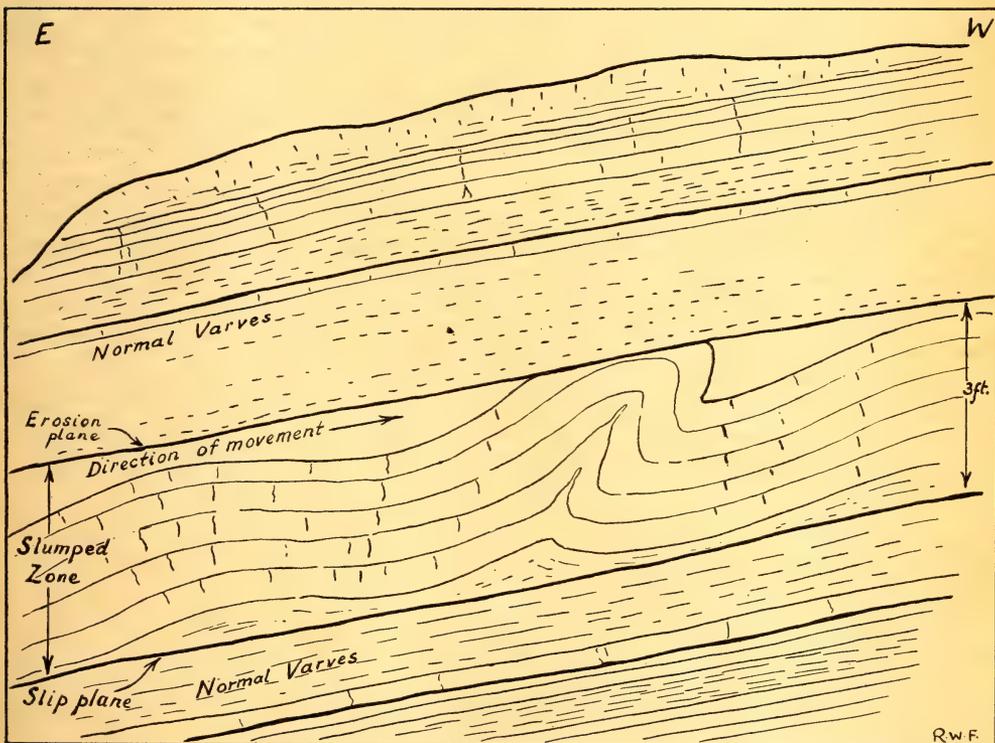


Fig. 1.—Characteristic slumped zone in Carboniferous varves at Seaham Quarry, N.S.W. Such perfect form is only obtained by movement in coherent, yet highly mobile strata. Note that the quarry face here is at about 45° to the direction of slump. The dip is about 30° S.S.W., while the slip occurred on a slope directed from N.E. to S.W., i.e. roughly in the same direction, but before the introduction of the present steep slope by subsequent tectonic action. (From a photograph by the author; see also Plate III.)

to make a regional study, in order to work out a directional analysis of any significance. This, however, might be a fruitful project for the future.

- (b) Ribbon-like overfolds, grading into overthrusts and imbrications, or "schuppen" and miniature "nappes" (using Alpine terminology). Generally only one annual layer is involved, often a fairly thick and competent one. The layer involved would belong to the year preceding that of the movement. This layer appears to have come "unstuck" and become folded over and piled up together, while the soft mud of the contemporary year fills in the loops and cracks. Folds and "schuppen" will range in this way up to about six inches in height. The beds above and below these are normal (see Fig. 2, and Plate IV).

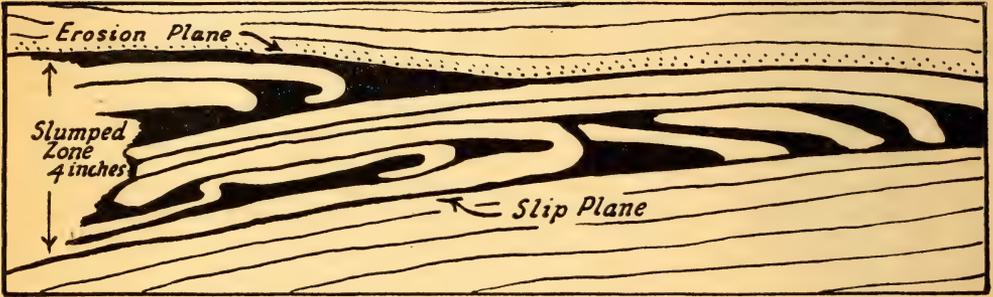


Fig. 2.—Ribbon-like overfolds and miniature "nappes" at Seaham. Note how the varve layers of particular years have become "unstuck" and moved more or less independently of one another. (From a photograph by the author; see also Plate IV.)

- (c) Fine layers of foreset beds with micro-contortions, usually not more than one inch high, between the normal beds above and below. These are therefore restricted to the contemporary year. Current scour, contemporaneous erosion and redeposition can be observed (see Fig. 3).
- (d) Zones of brecciation or injection, such as described first by Osborne (1925a), occur intercalated between normal strata in the same way as the first three structural types.

Experience overseas, in North America and Europe, together with a thorough examination of the literature, has suggested to the author that the type of structures encountered elsewhere in glacial varves is generally much the same. In addition to the four principal types listed above there are many associated or secondary types. The sliding block mentioned by Benson, for example, may be included here.

5. Distribution of the Structures.

From the distribution of these contemporaneous disturbances certain conclusions can be drawn:

- (a) The disturbances in a definite area appear to affect certain zones more than others. Higher and lower in the section, irregularities will be rare, until one comes to the next contorted zone. Browne, in particular, noted this interesting characteristic (1926).
- (b) A comparison of the regional sections by Sussmilch and David, Osborne, Carey and others, show that the disturbances in the varves do not occur at the same zone over any great distance, and will then switch suddenly to another zone, or die out altogether.

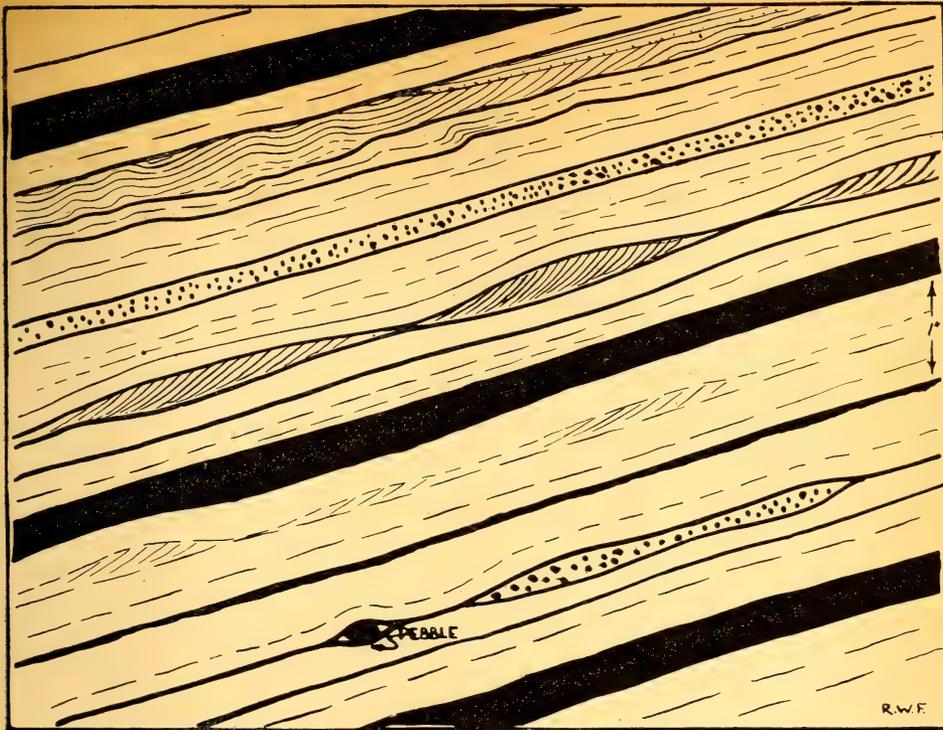


Fig. 3.—Fine layers of foreset beds with micro-contortions restricted to contemporary years, indicating local currents of temporary duration. (From a photograph by the author.)

- (c) The zones of disturbance in the varves do not reappear in any definite cycle. In some places they are overlain by tillites, but in others by great thicknesses of undisturbed varves, or by tuffs, mudstones or sandstones. This feature is most important, for, if the crumpling were due to glacial readvance, the contorted varves should always be overlain by a till, deposited by the retreating ice. It may be argued that the advancing ice pushed from one side, but this is quite impossible in these examples as neither over nor underlying beds are affected; alternatively, if the till that should theoretically be overlying the contorted horizon has actually been eroded away, no sign of this intense erosion is apparent, and no erosion relics are left.

III. REVIEW OF THE POSSIBLE CAUSES OF GLACIAL CONTORTION IN GENERAL.

In the expression "glacial contortion", we embrace all atectonic (i.e. non-diastrorphic), pseudo-tectonic and even some *apparently tectonic* disturbances in sediments associated in any way with glaciation. We shall deal with seven possible causes for this glacial contortion here. Amongst these a fairly wide field will be covered, even when it is quite clear in advance that certain ones cannot possibly apply to our Australian examples.

Examples of many of these types of glacial contortion are believed to exist in nature, though the relative importance of each may be hotly contested.

Certain other suggestions have been made from time to time regarding the origin of special cases of contortions in glacial beds, but the application of these

seems to be generally so infrequent or improbable that we cannot consider them here more than very briefly. For example, Emerson (1898) described certain little folds in the Pleistocene varves of Northampton, Massachusetts, as due to contemporaneous, subaqueous currents; considering his figure 39, we are certainly reminded of Lamont's current-induced "anti-dune structures" (1939). Emerson certainly seemed to be right here, but in another case, his figure 38, there is a most obvious case of slumping as we now interpret it, yet he said "The quiet water allowed the clay layers to form and then the strong current crumpled them" (*op. cit.*, p. 647).

And then again there was the suggested explanation by Shaler (in Shaler, Woodworth and Marbut, 1896, p. 969) for a four-inch bed of contorted clays which could be followed for over fifty feet in the Upper Merrimac valley (New Hampshire). Rightly rejecting glacial thrust, on account of the limited vertical range of the disturbance, he made the (then) rather novel suggestion that the sediments might have increased their bulk by some chemical reaction, such as the kaolinization of the clays. This chemical expansion process, called by Grabau (1924) "enterolithic", is now well known, but I doubt if it could be used to explain contortions in shale alone.

Lahee (1941) has included solifluction in his list of possible contemporaneous contortions, and unquestionably certain types of disturbance in glacial beds may be attributed thereto, though these would not normally be found in water-laid sediments, and in any case solifluction structures are often so characteristic that they are not usually mistaken for anything else. Nevertheless, certain structures known as "sticks" found below the German Pleistocene are ascribed to pre-Glacial leaching by Keilhack (1931), but are almost certainly due to solifluction.

A sort of differential creep has been envisaged by some authors. Sayles (1919, p. 38), speaking again of the New England Pleistocene varves and their contorted horizons, suggested a "creep toward an unsupported edge due to the weight of superincumbent clays alone". Miller (1922), who was a great exponent of differential drag as an explanation for many types of micro-tectonic structures, came to much the same conclusion about the same occurrences. Under the load of the overlying sediments, that is, by gravity, in a delta-fan for example, the more argillaceous beds are supposed to have crumpled and moved sideways while the sandier beds remained in place. In another place, Sayles (1919, p. 23) considered that differential shearing was produced at a lower horizon while a glacier ploughed through the beds several feet above. These concepts are hardly supported by the evidence; for one thing—in most of the New England varves there is but little lithological difference as a rule between the disturbed and the undisturbed layers. Further, the upper contact of the contorted zone is always a contemporaneous erosion plane with a local unconformity, and the overlying layer often shows an upwards grading from coarse to fine in the grains of sediment.

It is probably undesirable to spend more time on these rather exceptional cases, and so we shall now proceed to deal with the seven most usual explanations, more or less in the order in which they have become generally known.

They are as follows:

1. The grounding of ice-floes and icebergs.
2. The push of glacial readvance.
3. Post-glacial tectonics and differential movements.
4. Melting of frozen mud and "dead ice".
5. Disturbance due to subglacial dragging.
6. Structures preserved by englacial melting.
7. Gravitational slumping.

1. The Grounding of Ice-floes and Icebergs.

This was the first and still is the most popular explanation ; it was suggested by James Geikie (1874), and possibly even earlier authors. The idea is that drifting or wind-driven ice-floes or icebergs scrape along the sea or lake floor, rumpling the fresh sediments and displacing some of them. Stockton (1890) observed such grounding of ice-floes on the shores of Arctic seas. Priestley, on the Scott Antarctic Expedition, noted how the fauna on the sea floor near the shores was completely obliterated by the effect of grounding ice. Kindle (1924) reproduced a photo showing folds three feet high on the Arctic shores of Alaska. Koch and Teichert have noted the powerful effect of Arctic winds on sea ice in Greenland and I myself have been impressed by them in Canada. The objection, however, to this phenomenon being applied as an explanation for the contortions in the varved shales of Seaham type is that there is no evidence of an external crushing force, but rather of an evenly-applied force, which must be internal, since the strata above and below the disturbance are not touched.

Perhaps the best known locality for intraformationally folded zones in seasonally banded clays is in the Connecticut Valley region of New England, U.S.A. (see, for example, works by Emerson, Shaler, Sayles and others). For the last fifty years, certainly, the most favoured hypothesis here for explaining these contortions has been that of "glacial grounding". Unquestionably, certain of these structures, which range from an inch or so up to 20 feet in thickness, are due to a variety of other causes, as will appear in due course, but the bulk of them show constantly repeated features, that absolutely preclude the possibility of physical contact with floating ice. For example, the contorted zone is often thin, of constant thickness, underlain by normal sediments (the plane of separation being one of mechanical disturbance), but smoothly cut off above by erosion and unconformably overlain by another series of normal sediments exactly parallel to those below. There is abundant evidence of contemporaneous disturbance in the sedimentation, current phenomena, cross-bedding and ripple-mark, but often none of mechanical impact. As a rule there is no deposit of boulder clay such as would be deposited by the melting ice which is supposed to have grounded on the lake floor.

In exceptional cases, however, there is a layer of boulder clay above the contorted varve horizon (see, for example, Sayles, 1919, fig. 1). At the Woodsville clay pit, New Hampshire, several zones have this overlying layer of till. Sayles says (*op. cit.*, p. 19): "It would appear as if an iceberg of considerable size had dragged over the bottom, destroying some layers, contorting many of those below, and leaving a deposit of till on the top and there pressing pebbles down into the folded bands."

In the bulk of cases where there is no till, Sayles admitted that "it is difficult or impossible to decide what caused the movement" (*op. cit.*, p. 38) though, in explaining some of the plates, he suggested that one could imagine for these cases that icebergs had tipped upside down and crumpled the varves with their clean, formerly upper surfaces: an ingenious explanation indeed. In any case, it is extraordinarily hard to visualize how the passage of an iceberg could scrape up and crumple a single zone, say four inches thick, over exactly the same horizon for hundreds of feet, and yet not disturb the underlying beds at all. In terms of alpine tectonics, this would entail the explanation of a superficial "décollement" (disharmonic folding) by means of a "traîneau éraseur": a patent impossibility. The occasional presence of pebbles and boulder clay above the contorted zone can quite satisfactorily be explained by any melting of floating ice, without requiring an actual mechanical collision (see, for example, Sverdrup, 1931).

Another series of typical intraformational contortions in laminated shales, similar to those at Seaham, but at Squantum, Massachusetts, has been described

by Lahee (1914) to be the result of grounding floe-ice, an idea accepted also by Sayles (1919). First, he said, the ice crumpled the zone and secondly more floes came along and neatly carved off the tops of the resultant folds. Sayles (1914) noted a current-bedded sandstone overlying them in one place and suggested that running water might have truncated the beds. As to the contortions themselves, in many cases no trace remains of the impact of grounding ice in the form of a compressed and macerated surface, or of boulders or lenses of tillite (such as would result from the melting of the ice-floe) in the immediate vicinity of the disturbances.

The age of these Squantum beds has been provisionally put as Permian or Carboniferous, but even this must not be regarded as more than a rough estimate, and it is possibly in part due to "wishful thinking", a desire to make it contemporaneous with the Permian and Carboniferous glaciations of the southern hemisphere (see Dunbar, 1924, and others). In fact, serious doubts have been cast by several authors (Köppen and Wegener, 1924, p. 33; van der Gracht, 1928, p. 221; Salomon-Calvi, 1933, p. 103) on the actual evidence for glaciation in the Squantum beds, pointing out that neither seasonal banding (contrary to Lahee's opinion, 1914), nor "tillite-like" boulder beds are absolute criteria for it. I would like to draw attention to a similar association of absolutely *non-glacial* sediments forming today at the Dead Sea in Palestine. Banded seasonal shales (Lisan marl series) are associated in places with enormous boulder beds, which are produced under seasonal arid conditions; and in associated mud-flows the boulders often receive pseudo-glacial striations.

Thus, in spite of claims made by J. Geikie, Chamberlin, Atwood, Lahee, Sayles, Twenhofel, Sussmilch, David and others, I do not believe any fossil example of this "glacial grounding" has been definitely proven. Slater, one of the greatest glaciologists in Britain today, has remarked (1926) that one of the chief errors of the so-called Agassiz school of glaciologists has been "the over-emphasis of floating ice as a geological agent". In spite of this warning, the error still persists, though the alternative possibility of gravitational slumping has received some rather tentative consideration in recent years, as shown, for example, by an illustration of typical intraformational folds in the Massachusetts Pleistocene varves "caused presumably by slump or the pushing of grounded bergs" (Jahns and Willard, 1942, pl. 2).

2. The Push of Glacial Readvance.

This is the next most popular hypothesis, postulating that, as a glacier readvanced, pushing into its own peri-glacial lakes and streams, both its end-moraine and its peripheral glacio-fluviatile and glacio-lacustrine beds would crumple. Twenhofel (1932, p. 748) suggests that there will be a zonation, grading away from the end of the glacial advance: "brecciation will be nearest the ice, succeeded outward by a zone of thrust-faulting and over-turned folds, and beyond this by a zone of low or gentle folding". Certainly end-moraines show this sort of disturbance (see Lamplugh, Reid, Slater, Lewis, Keilhack and Salomon), but I do not believe that any such zonation over large areas of water-laid sediments has ever been seen in nature. In a glacial readvance the preexisting beds would tend to become frozen solid, and neatly sheared off (Slater). Bailey pointed out that the snow and ice overlying frozen sediments would act as a gliding plane. The type of folding normally found in varves is open and free and the sediments seem to have been soft, saturated and mobile. An external pressure applied to any unconsolidated sediment cannot be transmitted far by that sediment. Maceration results, not folding.

3. Post-glacial Tectonics and Differential Movements.

As remarked above, we are dealing only with structures in beds of glacial origin, water-laid or melted out from decaying glaciers that appear to be atectonic (i.e. non-diastraphic). Yet some of these structures have been interpreted as resulting from post-glacial tectonics. In general this hypothesis is discounted, but in the North American Pleistocene certain of these structures, which we regard as definitely contemporaneous, have been described by Miller (1922) and others as due to differential tectonics, in one form or another.

First objection is the fact that the Pleistocene is remarkably free from tectonic disturbance and that a differential horizontal movement would require considerable orogenic forces or contrasted elevation (to permit gravitational down-sliding, also postulated by Miller). Secondly, the commonest types of intraformational disturbance in glacial sediments exhibit an erosion plane above the folding; differential movement would require a gradual transition or a definite slip plane here. Of all the possible causes of glacial contortion this type is regarded as the least probable. An example in western Canada, regarded by Allen as tectonic, has already been identified as due to glacial action (type 5, below) (Slater, 1926). Exceptional cases may be encountered in regions where the fractures of block-faulted zones continued moving while the sediments were still forming. Such is definitely the case in parts of eastern Europe (von Bubnoff, 1936, p. 1482) and in parts of North America (Mathew, 1894, etc.). In such cases the type of disturbance should be self-evident as a rule, and would not normally be confused with other types.

4. Melting of Frozen Mud and "Dead Ice".

The accepted explanation for certain intraformational contorted glacial beds has long been the melting of a sheet of intercalated frozen mud, producing internal collapse with some lateral readjustment (see mention in A. Geikie, 1903, etc.). Stagnant patches of "dead ice" eventually melt out, giving the same results. It is clear, however, that this method requires certain conditions which are not present in many of the contorted beds. For example, evidence of roof-caving and collapse should be obvious. Lateral slumping would only be associated with it as a secondary feature. Such an explanation could scarcely be considered for the examples in the Seaham varves, since the latter are firstly not of tillite material, and secondly, are overlain conformably by other varved shales.

5. Disturbance Due to Subglacial Dragging.

This would be a scraping movement in the style of the Alpine "traîneau écraseur". A glacial readvance is postulated, but a different mechanical process is involved. Instead of glacial push, we have a sub-glacial drag. We should expect to find a capping of boulder clay or till, which will melt out when the glacier retreats. The disturbance will be more like deep-seated tectonics with high angle thrusts and imbrications. Such phenomena are definitely found in nature. Here we have some of the glacial pseudo-tectonics which are so well known in the Pleistocene of Europe (e.g. von Bubnoff, 1936, p. 1481) and North America (e.g. Emerson, 1898; Antevs, 1928). To this class will be restricted those disturbances which affect the basement, or floor of the glacier. Examples of this were shown by Slater in Norfolk (1926), Suffolk (1927*a*), Germany (1927*b*), Denmark (1927*c* and *d*), Alberta (1927*e*) and elsewhere; and in Australia, at Bacchus Marsh, by Jacobson and Scott (1937). If boulder clay is involved, and especially if angular blocks of the country rock are found embedded in contorted boulder clay, then it is highly probable that there has not only been subglacial drag, but also englacial melting (see below). In fact, the two are practically inseparable.

6. Structures Preserved by Englacial Melting.

This is a fairly modern theory based on the observation of contortions in the actual ice of glaciers themselves, which have developed during the laminar movement of the ice sheet (Hamberg, 1908 ; Phillip, 1920). In the advance of glaciers, material scraped off the floor is carried forward and upwards ; the flow movement of the glacier produces contorted folds and overthrusts within itself very similar in appearance to those of Alpine tectonics. It is argued that, when the glacier melts, this material is deposited *in situ* and preserves the same contorted structures. The material will consist of boulder clay (till), plus exotic blocks carved off from the irregularities of the glacial floor and carried up along the thrust planes within the glacier. In boulder-clays and tillites, therefore, we may expect to find these pseudo-tectonics or "fossil glaciers" (Chamberlin, Phillip, Gripp, Slater, Richter, etc.). Since glacial flow is conditioned by gravity, the type of tectonics will emulate that found in the superficial Alpine folding, though some deeper-seated tectonics are also to be expected, as a result of subglacial drag. Frequently imbrications of the country rock, Cretaceous, Eocene, Oligocene and Miocene, are involved with the Pleistocene glacial materials (Geikie, Kayser, Keilhack, Wahnschaffe, Slater, Shaler, Woodworth, Veatch). Exotic blocks encountered under these conditions in north Germany occur up to half a mile in length. Slater describes them in England as "giant erratics". In both north Germany and North America, complex folding, shearing and thrusting are found parallel to the old morainal fronts in the Pleistocene englacial material.

Water-laid sediments will not be encountered in this englacial material unless it is in the form of these "exotic blocks". There is no doubt that our undisturbed varved clays, with clear evidence of seasonal deposition and contemporary life, were water-laid and therefore could not have been involved in these glacial pseudo-tectonics. An example of this englacial melting, however, with exotic masses of water-laid varved rock introduced into the till, is noted, and correctly interpreted by Carey (1937, p. 358) from the Werrie Basin, N.S.W. Another example was recorded at Bacchus Marsh (Permian) by Jacobson and Scott (1937). It appears likely too that the contorted patch of glacial sands intercalated in the tillites on the Finke River, S.A., described and illustrated by David and Howchin (1923), belong to this group. These authors ascribed the disturbances to a glacial push, but Ward (1925) regarded the associated contorted tillites as englacial melts. Sayles (1914) described how fragments of the varved slates at Squantum are now found in the overlying "till". This he interpreted as subglacial dragging, but a laminar movement of the ice-sheet followed by englacial melting could just as well have brought it into its present relation with the "till". Easier still, ordinary sedimentary conditions could have produced this relationship.

Mention should be made at this point of the Carruthers hypothesis (1939). Carruthers believed that the "banded clays" and varved rocks of Britain were not water-laid, but were boulder clays, given a false stratification by the laminar movement of glaciers, which had subsequently melted. Melting is supposed to start at the base and work upwards. In this way, he argued, perfect pseudo-morphs of the internal structure of glaciers would be preserved in those banded clays and silts, which are normally attributed to glacio-lacustrine deposition. This hypothesis was most thoroughly examined, discussed and eventually rejected by the bulk of speakers at a meeting of the Geological Society in London. The discussions, however, served to show that the bulk of the glacio-lacustrine contortions were regarded by Bailey, then Director of the Geological Survey of Great Britain, and other competent speakers, as typical gravitational slumping phenomena. And this leads us logically to our last type of contortion in glacial beds.

7. Gravitational Slumping.

Gravitational slumping takes place in water-laid glacial deposits under penecontemporaneous subaqueous conditions. As noted above, when Carruthers displayed photos of certain contorted glacial beds to the Geological Society in 1939, Bailey, Trotter and others immediately pronounced them to be gravitational slides, "exactly comparable to the slump effects so well known in the geosynclinal Lower Palaeozoic rocks of Scotland and Wales" (see fig. 6b).

Hitherto the subject has received but little attention, although recognized in specialized conditions, such as the melting of the ice enclosing subglacial streams, when lateral slumping will occur in the resultant eskers (Flint, 1928). This fact is well recognized by de Geer (1940) in the "ose" (or esker) ridges of Sweden. Twenhofel (1932, p. 740) quite clearly says: "Glacial deposits not uncommonly are held up by ice against or over which they have been deposited. As the ice melts away, slumping takes place with possible deformation of the strata." However, most previous observers have attributed such contortions to one or other of the six possible sources of disturbance listed above.

Hadding, after making a thorough study of gravitational slumping in Sweden (1931, p. 390), noted evidence of it in the late Pleistocene there; he mentions how Munthe had attributed this particular folding to glacial readvance, but argues that this "may not be possible, after we have seen how structural forms of the kind present here are typical of subaqueously slid strata".

In his wonderful new study of the Swedish varves, de Geer (1940) definitely recognizes the rôle of slumping in causing local disturbances in his geochronological varve scales, for he says (p. 28), "Sliding of many or single varves has occurred especially where the slope was steep and when a locality became elevated above water-level and its counter-pressure thereby was annihilated. Sometimes the whole bunch of slidden varves has got their thickness falsified, sometimes the sliding has affected the lower varves only, while the upper ones have preserved their normal thickness." This phenomenon, however, was only recognized within narrow limits and many illustrations in his work are labelled as due to iceberg grounding, when the evidence is all for slumping. He recognized, however, that normally the grounding iceberg would leave a layer of till.

After naming half a dozen possible types of contemporaneous disturbance (including grounding ice-floes and icebergs, subglacial drag and solifluction), Lahee in his well-known textbook on "Field Geology" (1941, p. 192) also recognizes that saturated muds will slide at only 2-3°. "The resulting structure, though closely resembling the contemporaneous deformation due to grounding ice blocks, is likely to be of wider extent in the plane of stratification. Isolated boulders and other evidences for the former presence of ice might serve as a means of discrimination were it not for the fact that there is nothing to prevent mud flows in bodies of water in which icebergs are floating." As we have seen at Seaham in particular, there is a *notable absence* of erratic boulders or glacial débris in the vicinity of the contorted beds.

As far as I am aware no reference to the possibility of slumping in the lakes of the Glacial period in the north of England can be found before the 1939 discussions. In America, however, half a century ago, McGee (1891, p. 469) appears to have been the first to recognize it, when he attributed the contortions in the Pleistocene beds in Muscatine County, Iowa, to "inequipoential slipping . . . of the most readily yielding beds" (see Fig. 4). Other contorted beds there, however, showed the usual symptoms of our type 5 (subglacial drag) and these he recognized for what they were. Subsequent authors were not so observant, either ignoring the structures or attempting to generalize on one or other of our first six above-mentioned types. Miller (1922) performed a service by rejecting, point for point, No. 1 of these types (glacial grounding), but unfortunately only in an endeavour to prove a certain theory of his own

(differential movement), which is not supported by all of the observed facts in glacial beds.

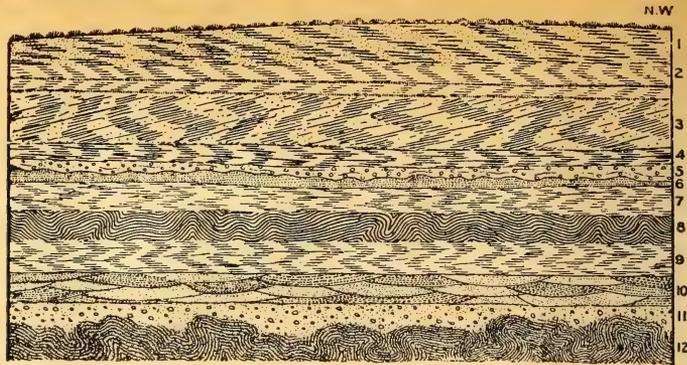


Fig. 4.—The contorted glacial beds which were first recognized as due to slumping. This section from Muscatine, Iowa, was drawn by McGee (1891, fig. 59). The contorted beds are well laminated silty clays of fluvio-glacial origin; the lower horizon is overlain by a gravel and the upper by a similar silty clay.

Slumping was apparently considered by Sayles (1914), for the Squantum contorted slates, but he did not have the advantage of having Arkhanguelsky's results of 1930 and did not appear to have considered the works of Heim (1908) or Hahn (1913). He remarked: "In view of the fact that the layers above and below the folds have not been deformed, it is difficult to see how the folds could have been formed by simple gravity, especially when it is noted that the folding and deposition were contemporaneous." As will be seen in the following, it is precisely these criteria which are characteristic of gravitational slumping.

Let us, then, review this slumping question.

(a) *General Conditions Required for Slumping.* It is found that submarine slumping is very common today, especially on steep lake floors, continental slopes, etc., and often under the stimulus of slight seismic vibrations. With suitable sediments (water-saturated intercalated muds and sands) Arnold Heim (1908) had observed that slipping on a large scale takes place on a lake slope of two to three degrees. As a result of extensive soundings and samplings with a coring tool in the Black Sea, Arkhanguelsky (1930) has even demonstrated

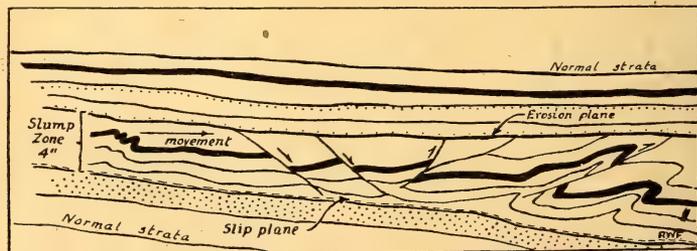


Fig. 5.—Contortions due to gravitational slumping, obtained artificially at the lower end of a 5-foot tank, tilted to only 7° . (In nature, on the grand scale, a similar effect is often obtained on an even more gentle slope.) After the irregular surface of the slumped beds had been eroded flat by the introduction of a slight current, it was then covered over by further sedimentation. Note juxtaposition of simple folds, overthrusts and tension faults.

slumping at under one degree in rather carbonaceous muds, but he found that sliding takes place *everywhere* in the soft superficial beds when the slope is over two or three degrees. Milne (1897) in studying submarine cable-breaks, demonstrated that slumping was often the cause and that it might take place on any slope of over one and a half degrees average declination. In the latest work on sedimentation, Kuenen (in Trask, 1939, p. 353) says, "as soon as this slope became more than a few degrees the deposits start to slide down".

The water actually supports the sediment in some cases, and slumping only sets in when that support is removed. Kindle (1917) observed contortions in the soft mud-flats of the Bay of Fundy in Canada, near the mouth of the Avon River. When I was there I noticed that when the tide went out the support was taken away from the newly deposited muds, and slumping set in. It was a striking coincidence when, without previous prompting, a keen local naturalist, Mr. Enright of Maitland, N.S.W., described to Dr. Osborne and myself just such a case of slumping in the bank of the Hunter River there many years ago after a high flood level had subsided. The slide has been subsequently hidden under a retaining wall to prevent similar slides.

Experiments have been carried out to show that slumping will actually take place in a laboratory tank, e.g. by J. Thoulet (1891, 1904) and more recently by R. E. Rettger (1935). Their results show structures that we know well in nature. Those interested should compare the photos of our supposed slumping in glacial beds with those of experimental slumps and some of the classical examples in nature, e.g. in the Ordovician at Trenton Falls, New York State (Hahn, 1913), near Girvan, Scotland (Henderson, 1935), and near Dublin, Ireland (Lamont, 1938); in the Silurian of Wales (Jones, 1939); in the Devonian of Gaspé, Canada (Logan, 1863); in the Jurassic of Sweden (Hadding, 1931); in the Solenhofen limestone of Germany (Walther, 1904); in the Tertiary of the Caucasus (Kugler, 1939); in the Miocene of Öhningen, Germany (Heim, 1908); and, most recently, in the Miocene near Florence, Italy (Beets, 1946). (See Figs. 6a, b, c, 7a, b, c.)

Here in Australia we have many examples of such contortions. In the Hawkesbury Sandstone in the Sydney region, these were attributed to slumping in the A.N.Z.A.A.S. "Handbook for New South Wales" (1932). This observation (by Dr. W. R. Browne, I believe) is the first actual reference to the Hawkesbury contortions as "slumping". Previous authors (e.g. Sussmilch, 1922, p. 161) say "no really satisfactory explanation of this feature has yet been suggested". Although nothing has been printed on the subject as yet, I understand that some years ago S. W. Carey prepared a short, unpublished paper on these structures in the vicinity of Long Bay, Sydney, as part of his university studies. Howchin (1920) found numerous examples of intraformational disturbances in South Australia (mainly in the Proterozoic) and recognized "subaquatic gliding deformation, which takes place on a gently sloping sea or lake bottom, by which the sediments become broken up, contorted and brecciated" (p. 307).

(b) *Summary of Criteria for Slumping.*—What do all of these structures have in common that distinguishes them from other small disturbances?

- (i) Contorted beds are intercalated between parallel undisturbed beds.
- (ii) The disturbances are on a small scale ranging from an inch or two to not more than 50 feet in amplitude.
- (iii) They do not usually show a *direct* connection with local tectonics, as, for example, does drag folding (see Nevin, 1936, for distinguishing features).
- (iv) Complicated folding takes place without well-developed associated cleavage.

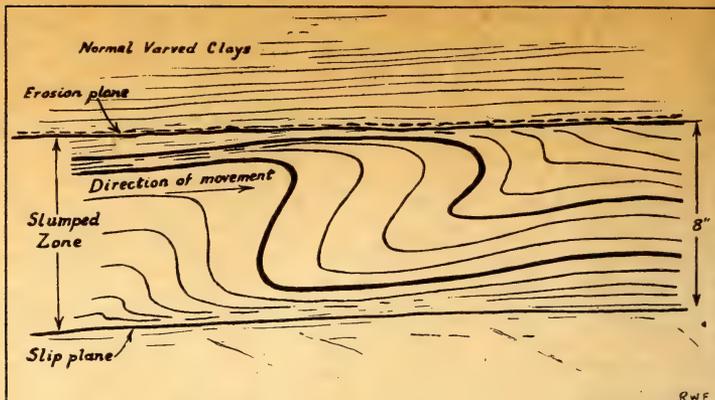


Fig. 6A.—Simple intraformational overfold in typical Pleistocene varved clays in the bank of the Connecticut River, two miles east of Northampton, Massachusetts. (From a photograph by Miller, 1922, fig. 5.)

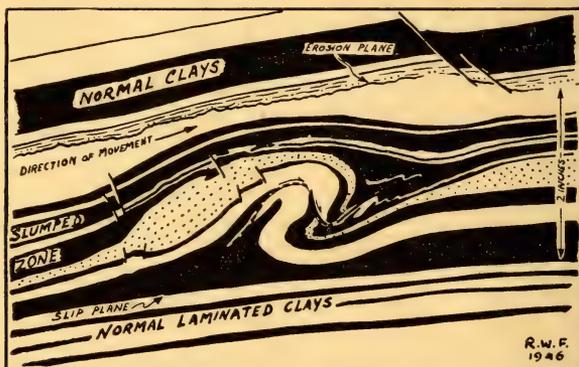


Fig. 6B.—Similar disturbance in the Pleistocene glacial clays of England (Coatham Stob, Durham). From a photograph by Carruthers (1939, Plate XXI, No. 4), of structures described by Trotter and by Bailey as "typical slumping". (See Carruthers, 1939, p. 330.)

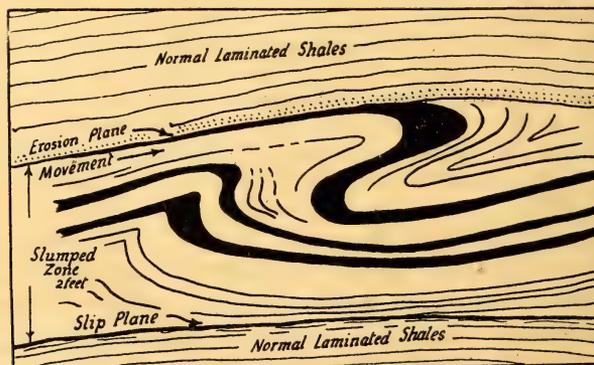


Fig. 6C.—Another similar disturbance, but this time in the non-glacial Lisan marls (Pleistocene) of the Jordan Valley, north of Jericho, Palestine. (From a photograph by the author.) The above drawings should be compared with out Fig. 1 and Plate III, showing similar structures in the Carboniferous varves at Seaham, N.S.W. Comparisons of this sort may be made with non-glacial slump folds from all parts of the world.

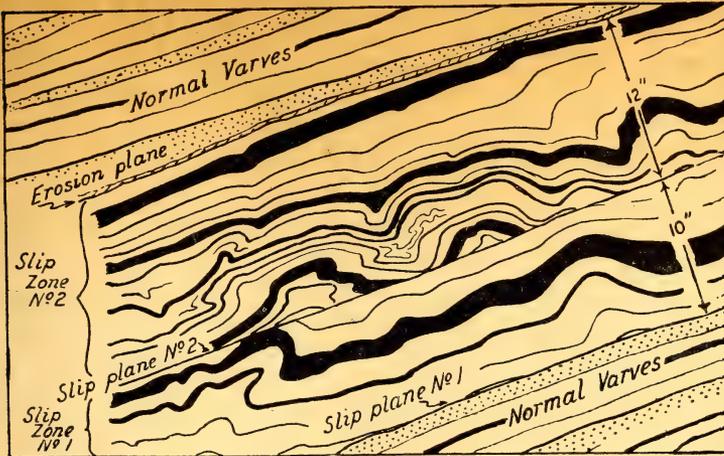


Fig. 7A.—Double slumped zone in Carboniferous varves at Cant's Quarry, Hillsborough, N.S.W. Slip zones numbers 1 and 2 are probably pencontemporaneous, but No. 2 has come from higher up the original slope, overriding No. 1. The section is almost certainly not at right angles to the original slope. Complex structural forms are due to the originally highly saturated nature of the beds. (From a photograph by Dr. W. R. Browne.)

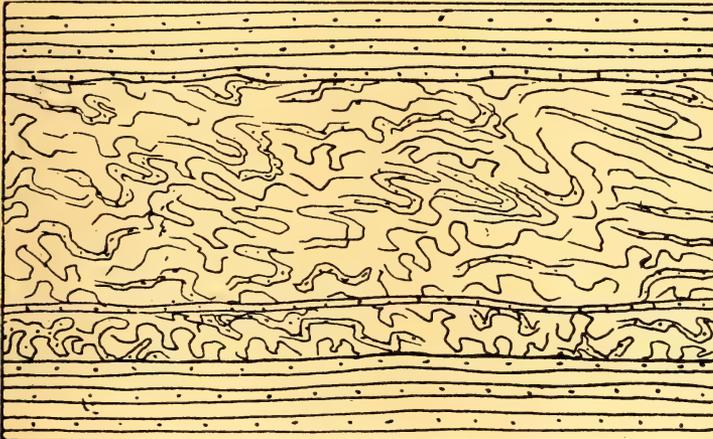


Fig. 7B.—Zones of contorted and dismembered beds in Pleistocene varved clays and silts at South Street clay pit, Northampton, Massachusetts. (From Miller, 1922, fig. 6.)



Fig. 7C.—Non-glacial example of fragmental "ribbon" contortions in Devonian limestones of Gaspé, Canada (after Logan, 1863, fig. 425). Now regarded as due to submarine slumping (Crabau, 1924; Twenhofel, 1932; and others). The slump zone varies from 7 to 10 feet in thickness.

- (v) Softer beds tend to flow into the gaps, brittle beds sometimes snap.
- (vi) There is no recrystallization or mineral orientation.
- (vii) The lower contact is normally a slip-plane.
- (viii) The upper contact is normally a local erosion plane.

While perhaps not all these criteria are always identifiable, at least the majority should be readily seen, even in fairly small outcrop. A regional survey of course should provide corroborative evidence.

(c) *Causes of Slumping in Glacial Beds.* Certain causes of gravitational slumping, as found in glacial beds, are restricted specifically to glacial conditions, while other causes of it may be encountered in any sedimentary deposits. It is generally simple enough to identify gravity slumping as such, but the precise identification of its cause cannot be seen from an inspection of the site alone, but requires a widespread regional study. We shall deal with possible causes in their probable order of importance in glacial beds.

- (i) A glacial lake is often dammed up by an ice wall; when the wall partly melts from time to time, the water support for the unconsolidated sediments will be removed and they will slump, only to be covered by more sediments when the ice returns and enables the water level to rise once more. The ice dam is often supplied by a glacier, which explains the apparent paradox that the water will actually return with a further cold period.
- (ii) In an ice dam formed by a moving glacier, open crevasses will come opposite the end of the lake from time to time and a certain quantity of water will suddenly escape into the opening, in the manner of steam into a slide valve. The release of water will cause a partial removal of support as in type (i) and smaller scale slumping will take place.
- (iii) Slumps will cause a sudden displacement of water at the bottom of the lake, setting up sudden currents, in the manner described by Sieberg (1927) for the origin of tsunamis in large-scale slumping (see also Gutenberg, 1939). Contemporaneous subaqueous erosion will be caused by these currents and the sediment removed will be redeposited and often slumped on an almost microscopic scale.
- (iv) A glacial stream debouches into a glacial lake building up a delta. Overloading will gradually occur and slumping will set in to restore the slope to its angle of rest.
- (v) Deposits in subglacial streams (later to form kames and eskers) will be supported as long as the ice lasts. As melting sets in the retaining walls will disappear and the unconsolidated sediments will slump outwards. Practically all kame and esker deposits are affected in this way (Flint, 1928).
- (vi) A glacial readvance may buckle and pile up the deposits at the head of the lake. These folds will not be transmitted to the further sediments as the material is as yet only partially consolidated. The pressure will cause the deposits nearest the glacier to rise up, thus providing a long outward slope, descending into the lake. Slumping will take place down this inclined plane.

(d) *Distribution of Slumping in Glacial Beds.* There appear to be large numbers of examples of slumping in glacial beds in the Pleistocene of Great Britain, Scandinavia and Germany, in Canada and the United States (illustrations, variously interpreted, may be found in Carruthers, 1939, see our Fig. 6b; J. Geikie, 1874; Wilson, 1918, see our Plate III; Miller, 1922, see our Figs. 6a and 7b; McGee, 1891, see our Fig. 4); in the Permo-Carboniferous in South

Africa and the Congo (Haughton, 1930 ; Fourmarier, 1916 ; Boutakoff, 1934) ; in the Carboniferous of New South Wales (Sussmilch and David, 1919) ; late pre-Cambrian of the Tien-Shan Mts. (Norin, 1937), and also South Australia (Howchin, 1920). Of these by no means all are restricted to varve shales ; some of the intraformational disturbances are in fluvio-glacial sands, some in glacial silts or stratified clays.

In the Kimberley Division of Western Australia, I myself noticed several horizons of these structures in the Permian sandstone cores from the Nerrima deep test-well of the Freney Oil Company in 1941. Raggatt (1936) has illustrated a contorted sandstone from the Lyons series (Permian) of the North-West Basin ; it underlies one of the glacial boulder beds (the boulders are believed to be dropped from floating ice), and Raggatt's conclusion was that the contortion "is clearly due to the pushing action of grounding ice rafts which deposited the boulders". He goes on to mention another example (there are many) in the bed of the Arthur River, where it is overlain by the Callytharra limestone. The sandstone is almost vertical, but the limestone dips at only 2-3°. Normal (conformable) relationships are seen a few yards upstream. In this case there is no evidence of débris from grounding ice rafts, and yet the contortion is the same. The first example, I would have considered as inconclusive, but the second may well be due to a slump phenomenon.

8. Criteria for Distinguishing Different Types of Disturbance in Glacial Rocks.

For general purposes, a few simple rules may be suggested for distinguishing the various disturbances encountered in glacial deposits :

- (a) If contorted beds are *englacial* (not water-laid), e.g. boulder clay or till ("Primary" of Slater, 1929, p. 457), the disturbance will be due to :
- (i) The push of glacial readvance (contortion adjacent to, or overlain by till).
 - (ii) Subglacial drag (contortion overlain by till).
 - (iii) Englacial shearing and subsequent melting (contortion in the body of, or at base of a till).
- (b) If contorted beds are *subaqueous* sediments, e.g. glacio-fluviatile, glacio-lacustrine, eskers, etc. ("Secondary" of Slater, *loc. cit.*), the disturbances will be due to :
- (i) Grounding of ice-floes, etc. (contortion adjacent to, or overlain by till).
 - (ii) The push of glacial readvance (contortion adjacent to or overlain by till).
 - (iii) Subaqueous slumping (contortion overlain by penecontemporaneous, water-laid material of some sort).

IV. CONCLUSIONS.

When we compare the features of the principal intraformational folded beds of Seaham, New South Wales and elsewhere in Australia, described in earlier papers and referred to in Section II of this paper, with the seven different possible types of glacially contorted beds, we are forced to reject each, on one count or another, until we come to the last. And our conclusion may be stated quite simply thus :

The bulk of intraformational folded beds in the Carboniferous of Australia exhibit recognized characteristics of gravitational slumping and relatively few suggest direct glacial impact. The slumping is very likely due to the periodic release of water from impounded, glacial lakes, overloading, and other well-recognized causes.

V. ACKNOWLEDGMENTS.

I am glad to be able to acknowledge my indebtedness to Dr. G. D. Osborne, first and foremost, for having so kindly conducted me to the finest outcrops of contorted varves in Australia, possibly, I believe, in the world; and then to Dr. Curt Teichert for plentiful encouragement, advice, and the loan of photographs; to Dr. S. W. Carey for interesting discussions; to Dr. Rosa Temko, of Perth, for assistance in the translation of many pages of Russian (Arkhanguelsky's important work).

Some of the material for this paper is taken from my D.Sc. thesis submitted to the University of Western Australia. It was with the kind advice of one of my examiners, Professor E. S. Hills, of Melbourne, that this work was undertaken.

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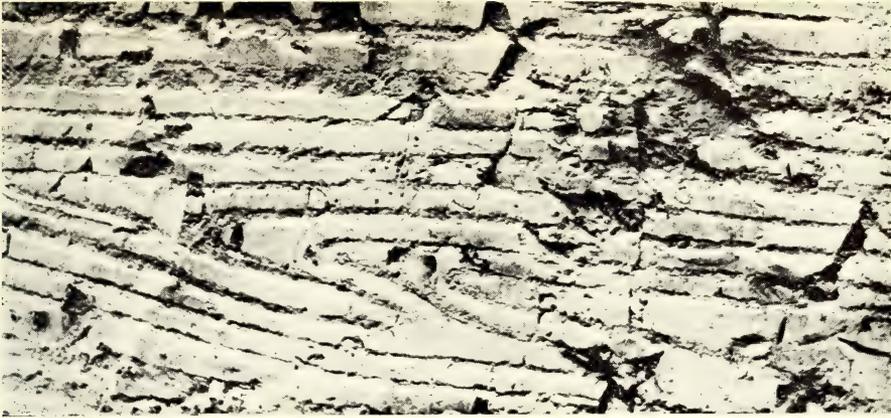
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EXPLANATION OF PLATES.

PLATE III.

Fig. 1.—Simple slump fold in Carboniferous varves at Seaham, N.S.W. (Photo. by Dr. C. A. Matley.)

Fig. 2.—Simple "ribbon" overfold (about $1\frac{1}{2}$ inches thick) affecting little more than one varve layer, at Seaham, N.S.W. (Photo. by the author.)

PLATE IV.

Fig. 1.—Simple slump fold in Pleistocene varves in Ontario, Canada. (From Wilson, 1918, Pl. XV.)

Fig. 2.—Another slump fold in the Carboniferous varves at Seaham, N.S.W., which compares closely with Fig. 1. Note simple fold (F.), ribbon structures (R.), unconformity (U.), and normal overlying varves (N.). (Photo. by the author.)

THE TEACHERS OF GEOLOGY IN AUSTRALIAN UNIVERSITIES.*

By H. S. SUMMERS.

INTRODUCTION.

I must first thank the Council of the Royal Society of New South Wales for the honour it has done me in inviting me to deliver the Clarke Memorial Lecture for 1947. There is no need for me to say anything about the man whose work we commemorate this evening, as previous lecturers have given far better accounts of the work and influence of the Rev. W. B. Clarke than I am capable of giving.

The choice of a subject for a lecture such as this is always difficult, as one must try to interest the professional geologist as well as others not so highly qualified, though extremely interested in the subject. In the present case the difficulty was accentuated by the fact that the lecturer has retired from the teaching of geology and has had his time so fully occupied with other matters at the University that no time has been devoted to either reading or research. I had almost come to the point of refusing with regret the invitation until I thought that a historical account of the earlier teachers of geology in Australia might well be of general interest. I therefore suggested the title of "A Geologist Looks Back", but found on gathering material together that there was no suitable point to end such a historical survey except at the present day, so this geologist has not only to look back, but also to look on the present. Hence I beg leave of the Council to amend the title to "The Teachers of Geology in Australian Universities".

Sydney is the oldest University, but not the oldest in teaching geology, since geology as part of Natural Science was first taught in Melbourne in 1854 by Professor McCoy, whereas in Sydney A. M. Thomson was not appointed Reader in Mineralogy and Geology until 1866. The University of Tasmania, though established before those of Queensland and Western Australia, had no properly organized teaching of geology until 1946, when the first Professor, S. W. Carey, was appointed.

It is interesting to note that the three older Universities are named after the capital city of the State—Universities of Sydney, Melbourne and Adelaide—while the three younger ones have been named after the State to which they belong—Universities of Tasmania, Queensland and Western Australia.

In all the Universities changes in the titles of the heads of the Geological Departments have taken place, but Sydney shows the greatest variety of names of Chairs, etc.

The first appointment in Sydney was that of A. M. Thomson in 1866 as Reader in Mineralogy and Geology, but the title was changed to that of Professor of Mineralogy and Geology in 1870. After Thomson's death Archibald Liversidge was appointed Professor of Geology and Mineralogy and later became, in addition, the William Hilton Hovell Lecturer in Geology and Physical Geography.

In 1882 W. J. Stephens was appointed Professor of Natural History and took over part of the work previously taught by Liversidge, and Liversidge's

* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, July 17, 1947.

Chair was renamed "Chair of Chemistry and Mineralogy". These two Professors shared the title of William Hilton Hovell Lecturer in Geology and Physical Geography. The next change was in 1890, when Stephens became Professor of Geology and Palæontology instead of Professor of Natural History and Liversidge became Professor of Chemistry. The next change took place when T. W. E. David was appointed, in 1891, Professor of Geology and Physical Geography and William Hilton Hovell Lecturer in Geology and Physical Geography. These two titles were subsequently combined, and on David's retirement the Chair was named the Edgeworth David Chair of Geology and Physical Geography and L. A. Cotton is now Edgeworth David Professor and William Hilton Hovell Lecturer in Geology and Physical Geography.

Compared with Sydney, Melbourne has been very conservative in its terminology of Chairs. Frederick McCoy was appointed in 1854 Professor of Natural Science. Though the name of the Chair was unchanged during McCoy's life, he was virtually Professor of Geology and Palæontology in the last few years of his life, all the non-geological work of the Chair of Natural Science being taken by Professors Masson and Spencer.

McCoy was succeeded by four Professors of Geology and Mineralogy—Gregory, Skeats, Summers and Hills.

In the University of Adelaide Ralph Tate was appointed Professor of Natural Science in 1875. On his death in 1901 the work in geology was divided between two lecturers, W. Howchin, Lecturer in Geology and Palæontology, and W. G. Woolnough, Lecturer in Mineralogy and Petrology. In 1904 Woolnough resigned and D. Mawson became Lecturer in Mineralogy and Petrology. In 1918 Howchin was made Honorary Professor of Geology and Palæontology, and on his retirement Douglas Mawson was made Professor of Geology and Mineralogy.

The University of Tasmania had geology as a subject for examination but there was in most years little if any teaching of the subject except during three years when the late A. N. Lewis was part-time lecturer in the subject. However, in 1946 S. W. Carey was appointed Professor of Geology.

Queensland commenced with a Lecturer in Geology and H. C. Richards was appointed in 1911, but in 1919 became Professor of Geology and Mineralogy and continued in this office until his recent death.

Western Australia commenced with a Professor as one of the Foundation Chairs and W. G. Woolnough was appointed Professor of Geology in 1912. After his retirement the Council decided not to appoint another Professor and E. de Courcy Clarke was appointed Lecturer-in-Charge of Geology but later was made Associate Professor and finally in 1930 he became Professor of Geology in the University of Western Australia.

I propose to deal with the Universities in order of age of establishment, and so will take Sydney first. In many cases, especially in the later appointments, it has been difficult to obtain all the information that one would have liked to include, and many members of the staff will not receive the notice that their position or research records would justify. To such persons I apologise.

SYDNEY.

The Act establishing the University of Sydney received the Royal Assent in 1850 and Sydney is thus the senior University in Australia. No appointment in geology was made until 1866, when A. M. Thomson was made Reader in Mineralogy and Geology.

Alexander Morrison Thomson was born in London in 1841. For a short time he attended the University of Aberdeen but soon returned to London,

where at King's College he won the Prize for Natural Philosophy. He graduated B.A. in 1861 and D.Sc. in 1867.

In 1870 the Readership was raised to the status of a Professorship and A. M. Thomson became Professor of Mineralogy and Geology. He only enjoyed the honour for a short time as he died in 1871 at the early age of thirty. Thomson had the distinction of being the first Professor of Geology in Australia because McCoy, who had held office for some years prior to Thomson's appointment to the Chair, was Professor of Natural Science.

In 1872 Archibald Liversidge was appointed Professor of Geology and Mineralogy.

Liversidge was born at Turnham Green, England, in 1847, and was educated at the Royal School of Mines, where he gained the Associateship of the School. He also trained at the Royal College of Science and at Christ's College, Cambridge. He graduated B.A. at Cambridge in 1885 and M.A. in 1887. The University of Glasgow conferred the Honorary Degree of LL.D. on Professor Liversidge. He was Scholar in Natural Science 1870-71-72 and was Demonstrator in Chemistry at the University of Cambridge in 1870.

The William Hilton Hovell Lectureship in Geology and Physical Geography was established in 1877 and Liversidge was the first Lecturer appointed.

Liversidge taught Chemistry as well as Geology and Mineralogy and in 1881 the Chair held by Liversidge was renamed Chair of Chemistry and Mineralogy. This change was made so that Liversidge could devote more time to Chemistry and the Geology was to be taken by W. J. Stephens, who was appointed Professor of Natural History in the following year. Nine years later, in 1890, a further change was made and Mineralogy was dropped from the name of the Chair and Liversidge became Professor of Chemistry and remained in this Chair until his retirement in 1908. Professor Liversidge died in England in 1927. Liversidge will long be remembered for his untiring efforts in the foundation of the Australian Association for the Advancement of Science and the part he played in helping to carry on the activities of that body. He was permanent Hon. Secretary from 1888 to 1909 and President of the Association at the meeting in Sydney in 1898. Other activities included Trusteeship of the Australian Museum, Hon. Secretary and three times President of the Royal Society of New South Wales. He was awarded the F.R.S. Liversidge was much more widely known as a chemist and mineralogist than as a geologist.

W. J. Stephens was appointed to the Chair of Natural History in 1882 and took over portion of the work previously done by Liversidge.

William John Stephens was born at Levens, Westmoreland, England, in 1829. He was educated at Haversham Grammar School, Marlborough College and Queen's College, Oxford, where he graduated B.A. in 1852 with First Class Honours in Classics and Third Class Honours in Mathematics and Physics. He was elected a Fellow and Tutor of his College. On the recommendation of Dr. Jowett, with whom he had been on friendly terms at Oxford, Stephens was appointed the first headmaster of the Sydney Grammar School, and held this position from 1856 till 1866. He then conducted a school of his own at Darlinghurst until his appointment to the Chair of Natural History in 1882. From the time of his appointment until 1888 Stephens shared with Liversidge the William Hilton Hovell Lectureship in Geology and Physical Geography, but from 1888 till his death in 1890 Stephens was the only Lecturer under this foundation.

In 1890 the name of the Chair was altered from Natural History to Geology and Palæontology, but Stephens only held this title for a short time as he died in that same year.

Stephens, as well as being an expert in Natural History was also an excellent Classical Scholar, and during portion of the years 1883-84 between the death of

Professor Badham and the arrival of his successor, Professor W. Scott, he was Acting Professor of Classics.

To fill the vacancy caused by the death of Professor Stephens, T. W. E. David was appointed to the Chair of Geology and Physical Geography and as stated above Liversidge's title was changed from Professor of Chemistry and Mineralogy to Professor of Chemistry. David also became William Hilton Hovell Lecturer in Geology and Physical Geography.

Tannatt William Edgeworth David was born at St. Fagan's near Cardiff, Wales, in 1858. He was educated at Magdalen School and at New College, Oxford, where he graduated B.A. in 1880. He first came to Australia to join the staff of the Geological Survey of New South Wales and soon showed his wonderful capacity for research. During this period he discovered and mapped the Maitland coal seams. He left the Survey on accepting the Chair of Geology at the University.

In 1897 David was leader of the party of scientists who visited the Ellice Islands, and there supervised the boring on the Funafuti Atoll. This work was carried out under the auspices of the Royal Society. The party, and also those who worked on the material in England, were required to record observations only and not to draw deductions. Among others who accompanied David were W. G. Woolnough of Sydney and George Sweet of Melbourne. E. W. Skeats and Frederick Chapman were two of those who worked in England on the material obtained from the bore cores.

During 1907-8-9 David was on leave and took part in Shackleton's Antarctic Expedition, and was the leader of the party that located the South Magnetic Pole and also led the party that ascended Mt. Erebus. During the first world war Major David organized and was O.C. of the Australian Tunnelling Co. He served from 1916 to 1919 and as Lt.-Colonel David was Chief Geologist to the British Armies on the Western Front. He retired from the Chair in 1924 and was made Professor Emeritus in recognition of his services to the University. He retained a room at the Geological Department and actively carried on research until his last illness. He died in 1934 at the age of seventy-six. Sir Edgeworth David had a wonderful personality and made friends wherever he went. During the latter part of his life he was the acknowledged leader of geology in Australia and was respected by all his colleagues. During the long period he was associated with the University, David travelled over most of Australia and collected an enormous amount of information on the geology of Australia and he was engaged before and during his retirement in writing up this material with a view to publication. The task was so great that it was far from finished at the time of his death.

David received many honours during his life, including C.M.G. (1910), D.S.O. (1918), K.B.E. (1920). Many Universities, including Oxford and Manchester, made him Honorary D.Sc. Wales and others made him Hon. LL.D. He was elected F.R.S. in 1900. Two Australian awards were the Mueller Medal in 1900 and the Clarke Memorial Medal in 1919. He was President of Section C (Geology) of the Australian Association for the Advancement of Science in 1892 at Hobart and again in 1895 at Brisbane. He was President of the Association in 1904 at Dunedin and again in 1913 in Melbourne. The honour of being twice President of the Association is shared with no other scientist.

During his period at the University of Sydney David saw many changes in staff. In his first year he constituted the whole staff, but with increase in the number of students so the number of members of staff grew.

The first appointment was that of William Smeeth, M.A., B.E., A.R.S.M., who joined the staff in 1893. Smeeth, who received his training at the Royal School of Mines, was also Lecturer in Metallurgy. In 1897 Smeeth resigned the

Demonstratorship in Geology and in the following year W. G. Woolnough, who had graduated B.Sc. in 1898, became Demonstrator, and continued in this position until 1901, when he was appointed Lecturer in Mineralogy and Petrology at the University of Adelaide. His record is discussed under Western Australia, where he was the first Professor of Geology.

In 1902 there were four new appointments :

A. H. S. Lucas, B.Sc., as Evening Lecturer in Physiography ;
Herbert Stanley Jevons, Assistant Lecturer in Mineralogy and Petrology ;
A. J. Peterson, B.Sc. (London), Demonstrator for the Lent term ;
W. S. Dun, as Lecturer in Palæontology.

The names of Lucas and Peterson occur in the University Calendar for only one year.

H. S. Jevons remained on the staff till the end of 1904, and W. S. Dun continued as Lecturer in Palæontology until 1934.

Herbert Stanley Jevons, M.A., B.Sc., was born in England in 1875 and was educated at University College, London, and Trinity College, Cambridge. He was Demonstrator in Petrology at Cambridge during 1900-01 and was Lecturer at Sydney 1902-04. After leaving Sydney Jevons drifted more and more towards Economics and was Professor of Economics at University College, South Wales, and later at Allahabad.

In 1906 T. Griffith Taylor was Junior Demonstrator, but left in 1907 with the Shackleton Antarctic Expedition. Though Taylor did little in the teaching of geology in Australia, he has made a name for himself as a geographer. Thomas Griffith Taylor, B.A., D.Sc., B.E., was Associate Professor of Geography at the University of Sydney from 1920 to 1928 and while nominally under Professor David was virtually independent. Taylor left Sydney to become Professor of Geography at the University of Chicago from 1928-1934 and transferred from Chicago to Toronto and still holds the position of Professor of Geography at Toronto.

In 1908 during Professor David's absence in Antarctica and again in 1923 when there was shortage of staff, Dr. C. Anderson filled the breach and was appointed Temporary Lecturer in Geology. Charles Anderson graduated M.A. at the University of Edinburgh and in 1901 was appointed to take charge of the Mineralogical Department of the Australian Museum. For his work there he was awarded the D.Sc. degree by the University of Edinburgh. Dr. Anderson was Director of the Museum from 1921 to 1940, when he retired.

In 1909 W. N. Benson was appointed Junior Demonstrator. Benson did a large amount of research work in Australia, but his main teaching has been done at the University of Otago.

William Noel Benson was born in Sydney in 1885 and received his geological training in the Sydney and Cambridge Universities. He was Acting Lecturer in Geology at the University of Adelaide in 1908, Demonstrator in Sydney 1909-10. During 1910-11 as an 1851 Exhibition Scholar he studied at Cambridge University and at several European Universities. He returned to Sydney and held a Linnean Macleay Fellowship from 1914-15. He was Acting Lecturer in the University of Sydney during 1916 and was appointed Professor of Geology at the University of Otago in 1916. He was elected F.R.S. in 1941.

In 1910 A. B. Walkom joined the staff as Junior Demonstrator but most of his teaching was done at the University of Queensland (see later).

In 1911 Leo A. Cotton, who had been appointed as Demonstrator in 1908, was appointed Assistant Lecturer and has remained on the staff ever since.

W. R. Browne joined the staff as Junior Demonstrator in 1912. Records of Cotton and Browne will be discussed later.

C. E. Tilley was Junior Demonstrator in 1916 and 1919 but has done very little teaching in Australia. He had his early training in Adelaide, where he

graduated B.Sc. in 1914. He then transferred to Sydney and took his B.Sc. Sydney in 1916 with First Class Honours and the University Medal in Geology and Chemistry. He was engaged in munitions work in England from 1916 to 1919, and in 1920 was elected to the 1851 Exhibition Scholarship from Sydney. During 1920-22 he carried out research work at Cambridge, where he graduated Ph.D.

Tilley was Lecturer in Mineralogy and Petrology at Cambridge from 1928 till 1931, when he was appointed Professor of Mineralogy and Petrology. He was elected F.R.S. in 1938.

L. L. Waterhouse joined the staff in 1917 as Acting Lecturer but came on the permanent staff in 1920 and is still a member.

Lionel Lawry Waterhouse was born at West Maitland in 1885 and was educated at Sydney High School and the University of Sydney, where he graduated B.E. (Mining) in 1909.

Prior to his appointment at Sydney he spent several years as Assistant Government Geologist and Inspector of Mines in Tasmania. Here he carried on excellent work under very adverse field conditions.

Waterhouse has for many years had charge of the courses in geology for engineers, which he has built up to a high standard, and his research and teaching have been almost wholly on the side of economic geology. He was promoted to the grade of Reader in 1946.

In 1923 E. C. Andrews was appointed an Acting Lecturer during Professor David's absence.

Ernest Clayton Andrews graduated B.A. (Sydney) in 1894 and was one of David's earliest students. He was a member of the staff of the Mines Department for many years, both as Senior Geological Surveyor and Government Geologist 1920-31, when he retired. Though he was not directly connected with the teaching of the subject for long, Andrews has done a great deal of educational work in geology both by means of published research work and by means of public lectures. He was awarded the Syme Prize in 1915. Andrews was the President of the A.N.Z.A.A.S. in 1930 at Brisbane.

He was awarded the Clarke Memorial Medal in 1928, the Lyell Medal in 1931, and the Mueller Medal in 1946. Andrews led the Commonwealth delegation to the Pan-Pacific Science Congress in Java, 1929; Canada, 1933; United States, 1939. He was the Silliman Lecturer at Yale University in 1927.

In 1924 a great change took place as Sir Edgeworth David retired and Leo A. Cotton became Professor in his stead.

Leo Arthur Cotton was born at Nymagee, New South Wales, in 1883, and was educated at the Fort St. School and the University of Sydney. He graduated B.A. with First Class Honours in Mathematics in 1906 and B.Sc. with First Class Honours in Mineralogy in 1908, in which year he was appointed Demonstrator in Geology. As a Linnean Macleay Fellow he carried on research work on the tin deposits of New England during 1909-10 and returned to the staff of the University as Assistant Lecturer and Demonstrator in Geology in 1911. As might be expected from his First Class Honours in Mathematics, Cotton's tendency in his research work has been largely towards mathematical and physical interpretations of geological phenomena, and in 1920 he was awarded the degree of D.Sc., his principal thesis being "Earthquake Frequency with Special Reference to Tidal Stresses in the Lithosphere".

In 1921 Dr. Cotton was made Assistant Professor of Geology, and held this position until appointed to the Chair in 1925. Among other activities Cotton was a member of the ship's party 1907-08 of the Shackleton Antarctic Expedition. He represented his University at the First Pan-Pacific Science Congress at Honolulu in 1920 and the Third at Tokyo in 1926. He was President of Section C (Geology) of the A.A.A.S. at the Hobart meeting in 1928, where he

gave a masterly discourse on the Causes of Diastrophism. During the war period he was Chairman of the Advisory Committee of Scientific Man Power (General), Chairman of the Mineral Resources Committee, Chairman of the Australian National Research Council, and Dean of the Faculty of Science. He has been a member of the Council of the Royal Society of New South Wales for some years and was President in 1929.

One member of the staff who had served long with David and continued as a Lecturer with Cotton was W. S. Dun.

William Sutherland Dun was born at Cheltenham, Gloucestershire, in 1868 and arrived in Australia the following year. He was educated at Newington College and studied geology at the University of Sydney, first under Professor Stephens and later under Professor David. He joined the Mines Department in 1890 and was for a short time assistant in the Hunter River area to David, who was then still a member of the Geological Survey of New South Wales. In 1893 Dun became assistant to Robert Etheridge, Junr., and under his guidance became an able palæontologist. In 1902 he became part-time Lecturer in Palæontology at the University and continued to hold the position of palæontologist to the Survey and for years was Honorary Palæontologist to the Australian Museum.

For many years W. S. Dun was the leader in his subject, especially in the Upper Palæozoic fauna of Australia, but more particularly that of New South Wales. His greatest interest was in the Lamellibranchs and the Brachiopods. He was President of the Linnean Society of New South Wales in 1913. He became a member of the Royal Society of New South Wales in 1908 and for many years was a member of the Council and was President in 1918. W. S. Dun died in 1934, in the same year as his friend and colleague Sir Edgeworth David, so that geologists and others, not only in New South Wales but in the whole of Australia, lost in the one year two men whom all felt honoured to call their friends.

Of the present members of the staff, W. R. Browne is the next senior to Professor Cotton.

William Rowan Browne was born at Lislea, Co. Derry, Ireland, in 1884, and received his early training in Ireland, but came to Australia and entered the University of Sydney, where he graduated B.Sc. in 1910 and D.Sc. in 1922. He first joined the staff as Junior Demonstrator in 1912, but the following year was appointed Assistant Lecturer and Demonstrator, and held this post until 1923, when he was appointed Assistant Professor. The title of Reader in Geology, which had been in abeyance since the time of A. M. Thomson, was again brought into use, and in 1939 W. R. Browne relinquished the title of Assistant Professor to become Reader in Geology in the University of Sydney.

From 1935 to 1939 Dr. Browne was relieved from his University duties to undertake the work of editing and preparing for publication the mass of MSS. which Sir Edgeworth David had accumulated on the geology of Australia, and at present is in England making arrangements for the publication of this important work. Dr. Browne has been twice President of the Linnean Society of New South Wales, in 1928 and again in 1944, and President of the Royal Society of New South Wales in 1932.

G. D. Osborne was first appointed to the staff as a Demonstrator in 1922, and but for one year has remained a member ever since.

George Davenport Osborne was born in 1899 at Sydney and was educated at Sydney High School and the University of Sydney, where he graduated B.Sc. in 1921 with First Class Honours and the University Medal. He was a Demonstrator from 1922 to 1924, when he was elected a Linnean Macleay Fellow in Geology. He held this Fellowship during 1925, but returned in 1926 to the

University as Lecturer and Demonstrator. In 1929 he was awarded the D.Sc. degree for research work, which was largely in connection with the structural features of the deposits of the Hunter River Valley.

In 1930 and again in 1938 Osborne was granted leave and went to England, where he gained the degree of Ph.D. in Mineralogy and Petrology at the University of Cambridge. Osborne was appointed Research Associate at Harvard University in 1939 and subsequently, with the award of a Carnegie Travelling Grant, visited many parts of Canada and the United States.

Dr. Osborne has had several years on the Council of the Royal Society of New South Wales, and was President in 1944. He has carried out extensive research on the Upper Palæozoic rocks of New South Wales with special stress on structural details.

Ida A. Brown joined the staff in the same year as Dr. Osborne, but has not had such continuous service.

Ida Alison Brown was born in 1900 in Sydney and was educated at Fort St. Girl's High School and Sydney University, where she gained her B.Sc. in 1922 with Honours in Mathematics and Geology and the University Medal in Geology. She was appointed Demonstrator in 1922. From 1927-1933 she held a Linnean Macleay Fellowship and carried out extensive field work in rugged country along the South Coast area of New South Wales. Her petrological studies showed that some rare rock types were present in the area. She was awarded the degree of D.Sc. in 1932 for this work.

Ida Brown was again Demonstrator in 1934 and was appointed Lecturer in Palæontology in 1935 in succession to W. S. Dun, and soon showed that she could change from a perfectly good petrologist to an equally able palæontologist.

Among the Demonstrators who have either at times been Acting Lecturers or have been on the staff for some years, the following may be mentioned :

Catherine Drummond Smith, B.Sc. 1911 (now Mrs. F. S. Cotton), was on the staff from 1912 till 1919.

Dorothy K. Powell, B.Sc. 1920, was a Demonstrator from 1920 until 1933, and was Acting Lecturer during Dr. Osborne's absence in 1931.

Florrie Quodling was first appointed a Demonstrator in 1924. She graduated in 1924 and is still a member of the staff. Miss Quodling was Acting Lecturer during W. R. Browne's absence in 1936-39, and some years ago was appointed Lecturer.

Germaine Joplin graduated B.Sc. in 1930 with First Class Honours and the University Medal and was appointed Curator of the Museum in 1931. In 1933 Miss Joplin was awarded a Junior Fellowship of the International Federation of University Women and studied at Cambridge, where she was awarded the Ph.D. degree for research work carried out in England. On her return she was Acting Lecturer from 1936 to 1939, and was in 1941 awarded a Linnean Macleay Fellowship in Geology. She carried out extensive field work and the necessary laboratory work on the igneous and metamorphic rocks of the districts around Cooma, Albury and other parts of New South Wales. Dr. Joplin at present holds a Teaching Fellowship at the University of Sydney.

J. A. Dulhunty graduated B.Sc. in 1938 with First Class Honours in Geology and was a Demonstrator during 1938-39. In 1940 he was elected a Linnean Macleay Fellow in Geology. He carried out extensive research into the occurrence and uses of torbanite and was awarded the degree of D.Sc. for this work. He has been on the Council of the Royal Society for some years and is the President for 1947.

In 1947 A. V. Jopling, B.E., B.Sc., was appointed Teaching Fellow in Geology.

Other graduates who have acted as Demonstrators and/or Curators include :
Fanny Cohen, B.A. 1908, B.Sc. 1909 ; Demonstrator 1909-11.

S. J. G. Davis, B.Sc., Demonstrator in 1913.

Olga Marian Pauss, B.A. 1912 (now Mrs. W. R. Browne). First Curator, 1913.

E. J. Kenny, who for many years was a member of the Geological Survey of New South Wales and later Assistant Under Secretary for Mines, was Demonstrator in 1917.

Doris Stilwell, B.Sc., was Curator for several years from 1917.

Harold Yates, B.Sc., was a Demonstrator in 1919. He has for many years been teaching Geology at the Ballarat School of Mines. He was awarded the degree of M.Sc. for research work in the Yass district.

Elaine Shepherdson, B.Sc. (now Mrs. Wilshire), Curator 1923-28.

Heather Drummond, B.Sc., Demonstrator 1925.

Jeanette E. Johnson, B.Sc. (now Mrs. Park), Curator 1929.

Alma G. Culey, M.Sc., became a Demonstrator in 1931 and was Acting Curator during Miss Joplin's leave.

Una A. Pickard, B.Sc. (Mrs. J. Black), Demonstrator 1935-37.

In 1938 Marion Breckenridge, B.Sc., was appointed Acting Curator, later Curator. The position is now held by Mabel Milthorpe, B.Sc.

A. J. Lambeth, B.Sc., was Demonstrator in 1939.

Joan Johnson, B.Sc. (now Mrs. D. G. Moye), Demonstrator in 1940.

Joan M. Crockford, M.Sc. (Mrs. G. Beattie), was appointed Demonstrator in 1942.

Mrs. J. Windridge, B.Sc., has been a Demonstrator since 1945.

Helen McRoberts, B.Sc., was Demonstrator in 1946.

Beryl Scott, B.Sc., and B. Champin, B.Sc., have been appointed Demonstrators for 1947.

The New England University College was established at Armidale in 1938 and A. H. Voisey was appointed in 1939 as Lecturer in Geology and Geography.

Alan Heywood Voisey graduated B.Sc. from the University of Sydney in 1933 with First Class Honours and the University Medal in Economic Geology, and M.Sc. in 1936. For several years he was a geologist attached to the Northern Territory section of the Aerial, Geological and Geophysical Survey of Northern Australia. In 1937 Voisey was elected a Linnean Macleay Fellow and continued the research work which he had begun while a student. His principal interest was in the relationship of the Carboniferous and Permian in north central New South Wales and their correlation with rocks of somewhat similar age in other parts of Australia. He visited Tasmania in 1938 to get first-hand knowledge of the Upper Palaeozoic deposits of that State. For his work on the Upper Palaeozoic Systems he was awarded the degree of D.Sc. in 1944.

Elizabeth M. Basnett (Mrs. A. Robbins), after a brilliant academic career, graduated B.Sc. in 1939 and M.Sc. in 1941. She was appointed Demonstrator at Armidale in 1941, and lectured there in petrology for five years. She was succeeded in 1946 by Miss Margaret J. Colditz, M.Sc., who was Acting Lecturer for a period of eighteen months.

MELBOURNE.

The Act to establish the University of Melbourne was assented to by the Governor in 1853 and the first Council was appointed in that year. The Council decided to ask a committee in England to select four Professors, and one of those chosen, Frederick McCoy, became the Professor of Natural Science.

Frederick McCoy was born in Dublin in 1823. He studied medicine first at Dublin and subsequently at Cambridge. Though he apparently qualified,

he was too young to be admitted to practice, and being offered a post as palæontologist in connection with the Geological Map of Ireland he drifted right away from Medicine and does not appear to have been admitted to any degree or to practice in medicine. As a result of his work in Ireland he published two large volumes containing descriptions with drawings of many new varieties of fossils. One volume was devoted to the Carboniferous Limestone Fossils of Ireland and the other to the Silurian Fossils of Ireland. Adam Sedgwick asked him to arrange the collections of fossils in the Woodwardian Museum at Cambridge and he was engaged on this work from 1846 till 1854. For a short time McCoy joined the English Geological Survey but left in 1850 to take the Chair of Geology and Mineralogy at the Queen's College, Belfast. He still carried on the work at the Woodwardian Museum during his vacations and the results of his work were published under the title of "British Palæozoic Rocks and Fossils". In 1855 McCoy commenced work in Melbourne as the Professor of Natural Science.

The foundation stone of the University was laid in 1854 but the buildings were not declared open until the 3rd October, 1855. The first Matriculation Ceremony took place and the first lectures were delivered in the Exhibition Building, but in the latter part of the year the work was transferred to the University.

At the time of his appointment McCoy held no University degree, but while in England on six months' leave in 1886 he was awarded the honorary degree of Sc.D. by the University of Cambridge and the M.A. degree by the Royal University of Ireland. On his return to Melbourne McCoy was admitted *ad eundem gradum* to the degree of D.Sc., being the first recipient of that degree in the University of Melbourne. Subsequently he was admitted *ad eundem gradum* to the degree of M.A.

During McCoy's absence the Rev. A. W. Cresswell, M.A., acted as his *locum tenens*. A. W. Cresswell had trained under McCoy and for some years was a member of the Board of Examiners in Natural Science.

Up till 1885 McCoy was expected to conduct three courses, one for each year of the Arts course. In the first year the subjects were Chemistry, Mineralogy and Botany, in the second year Comparative Anatomy and Zoology, and Geology and Palæontology were the subjects of the third year. The Chemistry had for some time been taken by John D. Kirkland, first as a Lecturer and later as a Professor of Chemistry.

In 1885 the Council decided that the subjects of the Chair of Natural Science were too broad and decided that Chemistry should be solely taught by Professor David Orme Masson, who was appointed to the Chair of Chemistry in that year. As it had been decided to establish a Chair of Biology, to which Walter Baldwin Spencer was appointed the following year, the Council further decided that Comparative Anatomy and Zoology should be divided between the Professors of Natural Science and Biology and that McCoy should retain the teaching of Geology and Palæontology. This arrangement did not last long, as in 1887 the regulation governing the degree of Bachelor of Science was passed and the grouping of subjects was altered. Natural Science was deopped from the Arts course and Geology, Mineralogy and Palæontology became subjects of the second and third years of the Science course. McCoy carried on nominally as Professor of Natural Science but actually as Professor of Geology until his death in 1899. Frederick McCoy founded the Museum of Natural History, and this was housed in the building now forming part of Union House. Later the bulk of the material was transferred to the National Museum in Swanston Street. McCoy was the Director of the Museum for forty-five years. In addition to his other duties McCoy acted as Palæontologist to the Geological Survey of Victoria and determined a large number of fossils collected by members of the Survey. He thus

helped to determine the ages and sequence of the various formations. The *Prodromus of the Palæontology of Victoria* is still a standard book of reference, as is also the *Prodromus of the Zoology of Victoria*. McCoy received many honours, among which may be mentioned F.G.S. (1852), F.R.S. (1880), C.M.G. (1886), K.C.M.G. (1891).

During McCoy's last illness and for the period between his death and the arrival of Professor Gregory the work of the Department was divided between T. S. Hall and G. B. Pritchard, both of whom had been taught by McCoy.

Thomas Sergeant Hall, M.A., D.Sc., was for many years the leading authority in Australia on the Graptolites. He became interested in this group while in charge of the Castlemaine School of Mines and after his appointment to the staff of the Biology School under Professor Spencer he continued his keen interest in this group of fossils and also carried on research on the marine Tertiary deposits of south-eastern Australia.

George Baxter Pritchard was for many years in charge of Geology, Assaying and Metallurgy at the Working Men's College (now the Melbourne Technical College). He was also attached for some time to the Chemistry School at the University as part-time Lecturer in Metallurgy. Pritchard's main interest was in the Mollusca, both Recent and of Tertiary age, and either as sole author or in collaboration with T. S. Hall or others, published numerous papers on Tertiary stratigraphy and palæontology.

The Chair of Natural Science having been changed to that of Geology and Mineralogy, J. W. Gregory in 1900 became the first Professor of Geology and Mineralogy in the University of Melbourne.

John Walter Gregory was born in London in 1864. He was educated at Stepney Grammar School and then entered the wool business in 1879 and remained in this occupation until in 1887 he was appointed an assistant in the Geological Department of the British Museum. While holding this post he found time to study Geology at the University of London and graduated B.Sc. in 1891 and D.Sc. in 1893. He remained with the British Museum until 1899 but while still on the staff spent some time in the Rocky Mountains and the Great Basin of the western States. In 1892-93 he was in British East Africa, the result of his work there being published as "The Great Rift Valley". In 1896 he accompanied Sir Martin Conway's expedition across Spitzbergen. Gregory spent less than five years in Australia but managed in that time to visit most parts of Victoria as well as to travel in other States. He took a party of students to central Australia during the long vacation 1901-02 and subsequently published "The Dead Heart of Australia". Though his views on the origin of the waters of the Great Artesian Basin are not accepted, as a result of his statements, opponents to his views brought to light far more information about this area than would probably have been obtained otherwise. In addition to his work as Professor he was freed part time from 1901 to become Director of the Geological Survey of Victoria and D. J. Mahony was appointed to relieve him of some of his duties at the University. Gregory left Victoria at the end of the second term in 1904 to take the Professorship of Geology at the University of Glasgow and Mahony carried on the work of the Department till the arrival of E. W. Skeats in 1905.

After leaving Australia, Gregory still found time to travel, and visited and explored Cyrenaica in 1908, Southern Angola in 1913, Chinese Tibet in 1922. In 1932 J. W. Gregory led an expedition to Peru and on the 2nd of June of that year was accidentally drowned in Urubamba River.

Daniel James Mahony, M.Sc. (Melb.), commenced an engineering course at the University, but due to the influence of Gregory he transferred to Science. Mahony joined the Geological Survey of Victoria as petrologist in 1906. He served in World War I with the Royal Artillery.

In 1931 Mahony was appointed Director of the National Museum. He died in 1946.

E. W. Skeats was appointed to the Chair of Geology and Mineralogy after the resignation of Gregory and arrived in Melbourne in February, 1905.

Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., was born at Southampton in 1875. He was educated at Handel College and Hartley College, Southampton, and at the Royal College of Science, South Kensington, where he gained a First Class Associateship in Chemistry in 1896 and in Geology in 1897. He graduated B.Sc. London in 1899 and D.Sc. in 1902, his principal thesis dealing with the origin of the dolomites of the Tyrol. Before his appointment to Melbourne Skeats was a Demonstrator at the Royal College of Science under Professor Judd. When Skeats took up his duties in Melbourne he was entirely responsible for the teaching of Geology and Mineralogy, but had an exceptionally able technical assistant in the late H. J. Grayson, who is more generally known for his fine rulings and the construction of a machine for ruling diffraction gratings. The Geology Department was at first housed in part of the original building of the University, but in 1907 it was transferred to a new building which had been erected to take Geology, Mining and Metallurgy. The amount granted for this building was insufficient and it was never very satisfactory. After the first world war extra temporary accommodation in ex-army huts had to be provided. As both Engineering, which adjoined the Geology Building, and Metallurgy required room for expansion, it was decided to provide a new Geology School, and this was officially opened in 1927.

With the growth of the School this building is no longer large enough and additions are being built at the present time.

Professor Skeats saw great changes during his long tenure of office from 1905 to 1940. When he first took up his duties Geology could be taken by second and third year Science students, second year Civil and Mining Engineers and third year Mining Engineers, and the Professor had to give lectures over one term in Physical Geography as part of a subject called Natural Science taken in the course for the Diploma of Education. Subsequently the Science Regulations were amended and Geology Parts I, II and III became subjects of the three years of that course. Natural Science ceased to be a subject of the Diploma of Education. Other courses taken now are Agricultural Geology, Geology Part I (Engineering Course), Geology Part I (Architecture Course) and Mining Geology. Skeats held many positions both within and without the University. He was Dean of the Faculty of Science, 1910-15; President of the Professorial Board, 1922-24; President Section C (Geology) A.A.A.S. in 1909 at Brisbane; and President of the Royal Society of Victoria, 1912-14. Professor Skeats was invited to deliver the first Clarke Memorial Lecture and later the first Edgeworth David Lecture. He retired in February, 1941, and in recognition of his services to the University he was elected Professor Emeritus of Geology.

Skeats built up a wonderful reputation for the School of Geology, and students who trained under him are to be found in important positions in many lands.

In 1906 two Caroline Kay Scholarships were first open to competition. These Scholarships were teaching Scholarships and had a tenure of two years. One of these was assigned to Geology and H. S. Summers was the first holder of a Caroline Kay Scholarship in Geology. This afforded some relief to Skeats, as Summers took over the lectures in Mineralogy and Petrology to the senior students. Caroline Kay Scholars who followed were required to demonstrate only. The names of the Scholars, in order of appointment, are as follows: H. S. Summers, D.Sc.; H. C. Richards, D.Sc., late Professor of Geology, University of Queensland; E. O. Thiele (now Sir Edmund Teale, D.Sc.), who has spent most of his life on geological surveys under the Colonial Institute;

F. L. Stillwell, D.Sc., now in charge of the Mineragraphy Section of the C.S.I.R. in Melbourne; M. Morris, M.Sc.; N. R. Junner, D.Sc., Director of the Geological Survey of the Gold Coast; C. A. Hoadley, M.Sc., who until his recent death was Principal of the Footscray Technical School; P. G. Towl, M.Sc., who was killed in action in World War I; and the last holder was Kathleen McInerny, M.Sc. (now Sherrard). In 1920 the University Council decided that the post of Assistant Lecturer would be established, provided that the Caroline Kay Scholarship in Geology was surrendered. The Scholarship is now the Caroline Kay Scholarship in Botany. Kathleen McInerny was appointed to the position of Assistant Lecturer and took over the lecturing on Building Stones and Road-Metals to Engineering and Architecture students.

Kathleen McInerny was admitted to the degree of Bachelor of Science in 1918 and of Master of Science in 1921. Miss McInerny was the first woman to graduate in Science at Melbourne, with Geology as a major subject. She was awarded the Caroline Kay Scholarship in 1918 and in 1920 became Assistant Lecturer in Geology. During 1929 Miss McInerny was granted leave of absence to visit England.

In 1920 Bertha Keastland graduated B.Sc. with Geology as her major subject and was admitted to the degree of M.Sc. in 1922. Miss Keastland was for many years attached to the Teachers' College, Melbourne, where she was in charge of students taking Geology at the University. During this period Miss Keastland frequently acted as part-time Demonstrator in Geology at the University.

In 1921 Frederick Chapman was appointed part-time Lecturer in Palaeontology.

Frederick Chapman was born in London in 1864. For some years he was assistant to Professor Judd at the Royal College of Science. During this period he became intensely interested in microorganisms, particularly, and in any forms of fossils generally. His book "The Foraminifera" was for long a leading textbook on this group of fossils. On the recommendation of Professor Gregory he was appointed Palaeontologist to the National Museum, Victoria, in 1902. During his stay at this institution he arranged and catalogued the collections and in addition figured and described a very large number of forms. From 1921 F. Chapman lectured and demonstrated in Palaeontology to students taking Geology, Parts II and III. In 1927 Chapman transferred from the State to the Commonwealth, but retained his room at the National Museum and also continued to lecture at the University. He retired from the position of Commonwealth Palaeontologist in 1935. He died in 1943.

In 1921 another important appointment was made. F. A. Singleton was appointed Lecturer in Agricultural Geology and Curator of the Museum.

Frederick Alexander Singleton was born in 1897 and was educated at the Melbourne Church of England Grammar School and the University of Melbourne. He was appointed a Lecturer in 1921 but two years later was made Senior Lecturer.

Singleton graduated B.Sc. in 1919, M.Sc. in 1921 and D.Sc. in 1940, in which year he also won the Syme Prize for Scientific Research. During Professor Hills' absence in England in 1946 Singleton was Acting Professor. In the same year Singleton was awarded the well-merited honour of being made Associate Professor of Geology, but unfortunately did not live long to enjoy the distinction and his death this year while still comparatively young robbed the University of an exceedingly zealous and efficient officer. Throughout his connection with the staff of the Geological Department Singleton was in charge of the Museum and the standard of his work in this connection is best shown by the paragraph in the report of Messrs. Markham and Richards to the Carnegie Corporation of New York on Museums and Art Galleries in Australia. On page 39 of this

report the following appears: "The Museum at the Geology School of the University of Melbourne has the best labelled and displayed geological collection in Australia and as a means of serving the purposes of the University, must rank very highly indeed in comparison with similar Museums throughout the world."

After the retirement of F. Chapman, Singleton had the work of lecturing in Palæontology added to his other work and until his death took this portion of the work in Geology Parts I, II and III. He also lectured to Part III on Australian Tertiary stratigraphy and on Fossil Man. Singleton was one of the leading palæontologists in Australia and was the Australian authority on the Tertiary Mollusca.

In 1923 H. B. Hauser, M.Sc., who had been a Junior Demonstrator, was raised to Senior Demonstrator and J. S. Mann, while still carrying on as Senior Technical Assistant, was given the additional rank of Demonstrator.

For several years from 1929 Ann Nicholls (now Mrs. Marshall) was a Demonstrator in Geology.

Ann Nicholls graduated B.Sc. in 1929 and M.Sc. in 1930. She was not only a Demonstrator in Geology but was also Tutor and later Assistant Lecturer in Economic Geography in the School of Commerce.

Miss Nicholls spent over a year in America studying Geography, first with T. Griffith Taylor at Toronto, and later in California. She also carried out research on soils in the Colac area in conjunction with Professor Wadham and Mr. Leeper.

In 1932 the Assistant Lectureship that K. McInerny had held was raised to a Lectureship and E. S. Hills was appointed to the post.

Four other men who were Junior Demonstrators for limited periods but who have since risen to high positions are:

Charles Fenner, D.Sc., who was later Principal of the Ballarat School of Mines and Lecturer in Geology, and is now Director of Education in South Australia.

Charles Wilson, D.Sc., who until his recent death was Director of the Geological Survey of Nigeria.

Arthur Lennox Conlon, D.Sc., and John Alexander Dunn, D.Sc., who have both recently retired from the Indian Geological Survey. Both rose to the position of Superintendent and both for some time were in charge of the Museum at Calcutta, which position also carried the post of Professor of Geology at the University of Calcutta.

With the resignation of Skeats in 1941, H. S. Summers was appointed Professor, but owing to age limitations only held the position for a very short period.

Herbert St. John Summers was born at Benalla in 1876 and was educated at the Carlton Grammar School (now extinct) and the University of Melbourne. There was a considerable gap between the time he qualified for Matriculation in 1890 and the time he entered the University in 1903. This time was largely spent in teaching in Queensland and Victoria. Summers graduated B.Sc. in 1905, M.Sc. in 1907 and D.Sc. in 1913. He first became a member of the staff as a Caroline Kay Scholar in 1906. He was appointed Assistant Lecturer and Demonstrator in Geology in 1909. This position was subsequently reclassified as Senior Lecturer. Several times during Skeats' absence Summers was appointed Acting Professor. In 1921 he became Associate Professor of Geology and in 1941 became Professor of Geology and Mineralogy, but resigned in 1944. Summers was a member of the University Council for twelve years from 1921 to 1935; President of the Royal Society of Victoria in 1931-32; President, Section C (Geology) A.A.A.S., Sydney, 1932.

When Summers became Professor some changes in the staff had to be made, but such changes were kept to a minimum so that his successor should have a freer hand. Previously Skeats had lectured on Mining Geology, so A. B. Edwards, of C.S.I.R., with the concurrence of Sir David Rivett, was appointed part-time Lecturer in Economic Geology.

Austin Burton Edwards graduated B.Sc. in 1930 at the University of Melbourne and showed even during his course evidence of the research spirit. He won an 1851 Science Research Scholarship and studied at the Royal College of Science and gained the Ph.D. degree at the University of London. He returned to Australia to join the staff of the C.S.I.R. in the Mineragraphy Section, which is housed in the Geological Department of the University. While carrying out mineragraphic investigations he found time to do extensive research work in General and Economic Geology. For his research work he was awarded the D.Sc. degree of Melbourne. He shared the Syme Prize in 1937.

Mention may be made here of Dr. F. L. Stillwell, who for many years has given several lectures per annum on subjects on which he is an expert to third year Science and fourth year Mining Engineering students.

Stillwell made a special study of Broken Hill, Bendigo and Kalgoorlie mining fields, but his major work has been the examination of ore and gangue minerals by reflected light on polished surfaces of the minerals. He has just returned from Fiji, having been asked to report on a microscopic examination of the ores with special reference to the tellurides. Stillwell graduated B.Sc. 1911, M.Sc. 1913, D.Sc. 1916. He was the Syme Prize winner for 1919.

Sylvia Bosselman was Demonstrator in Geology during 1939-40. Miss Bosselman (now Mrs. Whineup) obtained First Class Honours and the Exhibition in Geology right through her course. She is now Mineralogist and Petrologist at the National Museum, Melbourne.

In 1944 E. S. Hills was appointed Professor of Geology and Mineralogy.

Edwin Sherbon Hills was born in 1906 at Melbourne. He was educated at the University High School and the Universities of Melbourne and London. During his course at Melbourne he gained First Class Honours and first place with the Exhibition in Geology Parts I, II and III. He was placed first with First Class Honours in the M.Sc. Examination and won the Final Honours Scholarship and the Kernet Research Scholarship. He also held a Howitt Scholarship during 1928.

He graduated B.Sc. in 1928 and M.Sc. in 1929, D.Sc. in 1935. He acted as a Demonstrator for a short time in 1929 but being awarded an 1851 Scholarship went to London, where he won the Ph.D. degree. He was then offered a Lectureship in Geology at Melbourne and accepted the post and returned to Australia in 1932. In 1940 he shared the Syme Prize. In 1941 he was made a Senior Lecturer and an Associate Professor in 1942.

Hills is on the Council of the Royal Society of Victoria. He is Dean of the Faculty of Science and is the President Elect of Section P (Geography) at the A.N.Z.A.A.S. to be held in August of this year.

On the appointment of Hills to the Chair quite a number of changes were made in the staffing of the Department.

In 1944 the position of Senior Lecturer in Mineralogy and Petrology was filled by the appointment of C. M. Tattam, who commenced duties in 1945.

Charles Maurice Tattam was born in 1903 at Caulfield, and was educated at Essendon High School and the Universities of Melbourne and London and the Colorado School of Mines. He graduated B.Sc. in 1924 and qualified for the M.Sc. degree in 1925, but has never taken it out. In 1926 he went to the Royal College of Science and there gained the Ph.D., London. For some years he was on the staff of the Geological Survey of Nigeria and while on this staff he was given leave of absence on being awarded a Commonwealth (U.S.A.) Fellowship.

He took a course of geophysics at the Colorado School of Mines, where he was awarded the Sc.D. degree. He left the Survey to accept the Senior Lectureship at Melbourne.

Howard Bolitho Hauser was educated at the University High School and the University of Melbourne, where he graduated B.Sc. in 1920 and M.Sc. in 1924. He was appointed a Demonstrator in 1920 but was allowed leave in the latter part of the year to take a temporary Lectureship at the University of Western Australia, the vacancy having been caused by the resignation of Marcel Arousseau. He became a Senior Demonstrator in 1923 and on the appointment of Hills to the Chair he was made a Lecturer, his principal duties being lectures and demonstrations to classes in practical work.

George Baker, M.Sc., was born in Coventry, England, in 1908 and received his early education there. He came to Australia in 1925 and immediately got a position as junior assistant in the Geology School. After some time, as he had shown an aptitude for Geology, he was given time off to take the Science course and graduated B.Sc. in 1933. While still classed as a Technical Assistant he was appointed Tutor to Evening Students. He was so successful in this work that in 1945 he was made Lecturer and his principal duties are to lecture to evening students and to take charge of their practical work. He has done excellent research work and in 1935 gained the M.Sc. degree by research and in 1944 shared the Syme Prize for Scientific Research. He has always actively participated in the work of the Museum and at present is acting as Curator.

A. J. Gaskin was appointed a Lecturer in 1945. Arthur John Gaskin was educated at the University High School and the University of Melbourne. He graduated B.Sc. in 1940 and M.Sc. in 1941. Gaskin was a Demonstrator in 1941; then joined the C.S.I.R. laboratories at Fishermen's Bend, but returned to the University in 1945.

In 1945 Beryl Langham, B.Sc., who had previously been a Demonstrator, was appointed Research Assistant to Professor Hills and this was the first appointment of this type in the Geology Department, Melbourne.

Owing to the death of Associate Professor Singleton, a vacancy was caused on the staff, and this was filled by the appointment of Curt Teichert as Senior Lecturer in Palaeontology. Teichert holds the degree of Ph.D. of Königsberg and D.Sc. of Western Australia. He is an outstanding palaeontologist and was a Research Fellow for some time in the University of Western Australia, where he carried out some excellent work. He transferred to the Geological Survey of Victoria in 1946 as Assistant Government Geologist, but accepted the University post and commenced duties on the 1st of July, 1947.

ADELAIDE.

The University was established in 1874 and one of the Foundation Chairs was that of Natural Science.

In 1875 Ralph Tate was appointed to the Elder Professorship of Natural Science and was the sole member of the staff of this Department until his death in 1901. Assistant Examiners were appointed at times and J. Dennant, State School Inspector, Victoria, acted as Assistant Examiner in Geology on several occasions.

Ralph Tate was born at Alnwick, Northumberland, in 1840. He studied at the London School of Mines and taught at the London Polytechnic and at Mining Schools in Bristol and in Ireland. In 1864 he was made a Fellow of the Geological Society and appointed Curator of the Society's Museum. He was awarded the Murchison Medal in 1874 and next year took up his appointment in Adelaide. During his tenure of office he did a great deal to advance our knowledge of Geology, Botany and Zoology. He soon became an authority on the Tertiary palaeontology and stratigraphy of south-eastern Australia and figured

and described a large number of fossils from the Tertiary of Aldinga, South Australia; Muddy Creek and Mornington, Victoria; and Table Cape in Tasmania. He published many papers, principally in the *Proceedings of the Royal Society of South Australia*. In several papers J. Dennant was joint author. He was a member of the Horn Expedition to central Australia in 1894 and contributed to the scientific results of that expedition. Tate founded the Adelaide Philosophical Society. He was the first President of the Royal Society of South Australia. He was President of Section D (Biology) at the first meeting of the A.A.A.S. in 1888 in Sydney, and President of Section C (Geology) in 1900 in Melbourne.

Tate was President of the Association at the meeting held in Adelaide in 1893, and his presidential address dealt with a Century of Geological Progress in Australia. It is difficult for a palaeontologist or botanist to do any work in south-eastern Australia without having to look up Tate's views on the matter under investigation. During 1901, the year in which Tate died, the Council of the University divided the work of the Department as follows: Botany, E. L. Benham; Elementary Geology, J. D. Iliffe, B.Sc.; Advanced Geology and Mineralogy, I. H. Boas, B.Sc.; and Palaeontology, W. Howchin, F.G.S. J. D. Iliffe graduated B.Sc. in 1899 at Adelaide. Isaac Herbert Boas was born in Adelaide in 1878 and graduated B.Sc. in 1899 and in Western Australia graduated M.Sc. in 1916. For some years up to his recent retirement Boas was head of the Forest Products Laboratory of the C.S.I.R. in Melbourne.

The University Council decided not to make a fresh appointment of a Professor but to divide the geological work between two Lecturers, and in 1902 Walter Howchin was appointed Lecturer in Geology and Palaeontology and W. G. Woolnough Lecturer in Mineralogy and Petrology. Of these two, W. G. Woolnough is dealt with under the University of Western Australia, of which he was the first Professor of Geology.

Walter Howchin was born at Norwich in England in 1845 and was educated at the Academy, King's Lynn. Howchin was ordained a minister of the Primitive Methodist Church in 1865, but being more interested in geology than theology resigned from the ministry in 1880. He came to Australia in 1881 and was Lecturer in Mineralogy at the South Australian School of Mines from 1899 to 1904.

In 1902 he became Lecturer in Geology and Palaeontology at the University of Adelaide. In recognition of the high standard of his work the Council of the University in 1918 gave him the title of Honorary Professor. He resigned from the staff in 1920 but the Council asked him to retain the title of Honorary Professor.

Howchin was at first better known as a palaeontologist and published many papers dealing with this branch of geology. His later published work, however, showed that he had a wide knowledge of general geology and his presidential address to Section C (Geology) A.A.A.S. in Melbourne in 1913 was a masterly presentation of the physiography of South Australia. In recognition of his services to geology Howchin received the Clarke Memorial Medal in 1907 and the Mueller Medal in 1913. He was also the first to receive the Sir Joseph Verco Medal, which was awarded to him in 1929. Walter Howchin died in 1937 at the age of ninety-two.

W. G. Woolnough resigned the Lectureship in Mineralogy and Petrology in 1904 and Douglas Mawson was appointed to the vacancy.

Douglas Mawson was born in 1882 at Bradford in Yorkshire. He received his higher education at the University of Sydney, where he graduated B.E. (Mining Engineering) in 1901 and B.Sc. in 1902. In 1903 Mawson undertook geological exploration of New Hebrides and in 1905 he took up his duties at the University of Adelaide. He continued as Lecturer in Mineralogy and Petrology

until 1920, when on the retirement of Professor Howchin the two positions were combined and Mawson became Professor of Geology and Mineralogy, a position which he still holds. During 1907-08 Mawson was a member of Shackleton's Antarctic Expedition and in 1907 W. N. Benson took over his duties in Adelaide. While in the Antarctic, Mawson was with the party that fixed the position of the South Magnetic Pole and also took part in the ascent of Mt. Erebus.

In 1909 he was awarded the degree of D.Sc. (Adelaide) largely for research work dealing with the Broken Hill Mining Field.

Mawson then set about the organization of the Australian Antarctic Expedition, of which he was the leader. Professors David and Masson gave him much help in stimulating interest in this venture. Mawson was absent from 1911 to 1914, though some of the party returned earlier. During 1914-15 F. L. Stillwell was Acting Lecturer. Stillwell had accompanied Mawson to the South, but was one of those who returned early. In 1914 Mawson was knighted as a recognition of his successful leadership of an Antarctic Expedition. Shortly after the outbreak of the first world war Mawson was granted leave and went to England, where his services were utilized in the production of munitions. He was given the temporary rank of Hon. Major. In 1917 E. O. Teale was appointed Acting Lecturer. In 1920 Mawson was awarded the O.B.E.

Sir Douglas Mawson was the leader of the British, Australian and New Zealand Antarctic Expedition which during parts of 1929-31 explored the Kerguelen Island group and carried out extensive hydrographic surveys in the Australian Quadrant. Mawson received many medals in recognition of his explorations, including the R.G.S. Antarctic Medal in 1909, the R.G.S. Founder's Medal in 1915 and the King's Polar Medal with two bars.

In 1930 he was awarded the Mueller Medal and in the same year the University of Tasmania conferred the degree of D.Sc. on Mawson as a mark of appreciation of the work he had done in Antarctica. Notwithstanding his frequent absences abroad, Mawson found time to carry out original work on many parts of South Australia. He has published many papers, chiefly in the *Proceedings of the Royal Society of South Australia*. Mawson was President of Section E (Geography-History) in 1921 at the Hobart-Melbourne meeting and President of Section C (Geology) of the A.A.A.S. in 1926 at the Perth meeting, and President of the Association in 1935 in Melbourne, where he gave a full history of exploration in Antarctica under the title "The Unveiling of Antarctica".

Shortly after Mawson was elected Professor in Adelaide, C. T. Madigan was appointed Lecturer in Geology. This was in 1922, and Madigan still held the position at the time of his death in the early part of this year.

Cecil Thomas Madigan was born in 1889 at Renmark, South Australia. He was educated at the Universities of Adelaide and Oxford. In 1910 he graduated B.Sc. (Adelaide) but surrendered this degree in 1932 to receive instead the degree of B.E. He was selected as Rhodes Scholar for South Australia in 1911, but this was evidently held over as Madigan was a member of Mawson's Australian Antarctic Expedition, 1911-14.

During World War I Madigan served with the Royal Engineers, gaining his captaincy in 1916. He took part in the Battles of Loos, Somme, and Arras, was twice wounded and was mentioned in despatches.

Proceeding to Oxford, Madigan graduated B.A. with First Class Honours in Natural Science (Geology) in 1919. He took his M.A. degree in 1922 and in 1933 was awarded the D.Sc. of Oxford for his research work in South Australia. After leaving Oxford he joined the Sudan Civil Service in 1920, but resigned on being appointed Lecturer in Mineralogy and Petrology at the University of Adelaide.

Madigan was an active worker in little-known parts of central Australia and led excursions on several occasions to this area. He made an aerial reconnaissance of portion of central Australia in 1929, paying particular attention to the Lake Eyre district. He explored and geologically mapped portions of the MacDonnell Ranges, the Jervis Ranges, etc., and in 1939 was the leader of the Simpson Desert Expedition.

He summarized his researches on central Australia in his presidential address to the Geography Section of A.N.Z.A.A.S. in 1937 at Auckland, but has published further information since that date.

During World War II Madigan was given leave of absence from the University and was Chief Instructor at the School of Military Engineering near Liverpool, New South Wales. He was made Lt.-Colonel in 1941 but in 1942 left the Army to return to his duties at the University of Adelaide.

Madigan received the King's Polar Medal in 1914 and the Murchison Grant of the Royal Geographical Society to aid him in his work of exploration.

Among his non-scientific activities was his interest in the Boy Scout Movement, and for some time he was Chief Commissioner of Scouts for South Australia and was the leader of the South Australian contingent to the Jamboree in Melbourne. Madigan died early in 1947 at the age of fifty-eight years.

In 1930 A. R. Alderman was appointed Evening Lecturer in Geology at Adelaide.

Arthur Richard Alderman was born at Glenelg, South Australia, in 1901. He was educated at St. Peter's College, Adelaide, and the Universities of Adelaide and Cambridge. He graduated B.Sc. Adelaide in 1924 and M.Sc. in 1928. At Cambridge, Alderman entered Clare College and was awarded the Ph.D. degree for research carried out at Cambridge. In 1937 Alderman was appointed Research Assistant, and while holding this position carried on his research activities in petrology and on meteorites. Shortly after the outbreak of World War II he was seconded to the Division of Industrial Chemistry of the C.S.I.R., which had established laboratories at Fishermen's Bend, Melbourne. He has now resigned his appointment at Adelaide and joined the permanent staff of the C.S.I.R. Alderman was admitted to the degree of D.Sc. Adelaide in 1943.

From 1939 A. W. Kleeman has been Lecturer in Geology, first as Evening Lecturer and later as full-time Lecturer. Kleeman graduated B.Sc. Adelaide in 1933 and M.Sc. in 1935. He was appointed to the Aerial, Geological and Geophysical Survey of North Australia in 1936.

In 1946 Aleck William Whittle, B.Sc., was Evening Lecturer and in 1947 Allan Frazer Wilson, M.Sc., was appointed a Temporary Lecturer and Donald Ralph Bowes, B.Sc., was appointed Demonstrator.

Hector Brock, who for many years has been Chief Technical Assistant, is now ranked as Demonstrator and Technical Assistant.

TASMANIA.

The Act to establish the Tasmanian University, as it is called in the Act, was assented to in 1889 and three lecturers were appointed in 1892. These lecturers were later made professors. In 1896 details of Geology I in the second year of the Science course and Geology II in the third year were published. In 1903 details for Geology Parts I, II and III appear—Geology I being taken in the first year of the Science course, but there does not appear to have been any formal instruction provided. In the Calendar for 1899 William Alexander MacLeod, B.A., B.Sc. (N.Z.), is named as Lecturer in Chemistry, but remained on the staff for a very short time because in 1901 Peter James MacLeod, B.A., B.Sc. (N.Z.), was appointed Lecturer in Chemistry, Assaying, etc., and W. A. MacLeod is not mentioned. Both the MacLeods took out the B.A. from the University of Otago (N.Z.) in 1895 and W. A. MacLeod took the B.Sc. in 1897,

so that the B.Sc. after P. J. MacLeod's name was an error and does not appear in subsequent Calendars. P. J. MacLeod remained Lecturer in Chemistry, Assaying, etc., until 1905, when his title was changed to that of Lecturer in Chemistry and Geology and Fritz Joseph Ernst, B.Sc., was appointed Assistant Lecturer in Geology. F. J. Ernst graduated in 1904 and had evidently passed examinations in Geology, possibly under the tuition of P. J. MacLeod.

In the 1906 Calendar the name of F. J. Ernst again appears as Assistant Lecturer, but was noted as being on leave. No further mention of Ernst appears, although P. J. MacLeod's title remained that of Lecturer in Chemistry and Geology until 1915, when his title was changed to Lecturer in Chemistry. No further change appeared until the Calendar for 1918-19, in which the details for Geology Parts I, II and III contain the following notes :

“ After 1918 examinations in this subject will not be held until satisfactory arrangements can be made for the instruction of candidates.”

Conditions remained unchanged until 1926, when the note quoted above was omitted. In the following year new enlarged details for Geology Parts I and II were published but there was no mention of Geology Part III. In 1928 details for Geology Part III were again included and three part-time Lecturers in Geology were appointed :

Arndell Neil Lewis, M.C., LL.M. (Tas.).

Alexander McIntosh Reid.

Percival Bartlett Nye, M.Sc., B.M.E. (Melb.).

In 1929 a note appeared above the details for Geology II and III as follows :
“ At the time of going to press arrangements for lectures and laboratory work have not yet been completed. It is hoped that an announcement will be made at a later date.”

In 1930 no details were given for Geology II and III, though those for Part I were published. A. N. Lewis was, in 1930 and 1931, the only Lecturer in Geology.

A. McIntosh Reid and P. B. Nye were only on the staff for about a year, and both are better known for their work on the Tasmanian and other surveys than for academic work, so that no details of their training, etc., are given here. On the other hand no person has done as much to advance the teaching of geology in Tasmania as A. N. Lewis.

Arndell Neil Lewis was born at Perth, Tasmania, in 1897. He was educated at Leslie House School (now Clemes' College) and the University of Tasmania. At the University he studied law and graduated LL.B. in 1922, LL.M. in 1925 and LL.D. in 1930. Early association with R. M. Johnson laid the foundation of his interest in geology and while studying law he found time to take a wide interest in geology, more especially in respect to glaciation in Tasmania.

After graduating in Tasmania he went to Melbourne to do some extra reading in law, and while there attended as many classes in geology at the University as he could fit in. Arrangements were made for him to attend lectures and laboratory work in any of the courses in which he was interested and he attended all field excursions that were held during his stay in Melbourne. This extra work no doubt widened his knowledge, but he will long stand as an example of what can be done in self instruction by a person with brains, perseverance and enthusiasm. On his return to Tasmania he continued to extend his knowledge, especially of the glacial and physiographic features of the island, and soon became the foremost authority on Tasmanian glaciation. He served in the first world war, holding a commission (lieutenant) with the First Field Artillery, and won the M.C. After the war he served in the A.M.F., rising to Captain in 1924, Major in 1928, and Lt.-Colonel in 1933. Among other activities it may be mentioned that he was Chairman of Trustees of the Tasmanian Museum

and member for Denison in the State Parliament. He died in December, 1943, at the early age of forty-six.

In the Calendar for 1932 no provision was made for the teaching of geology, but details for Geology Part I appear.

No change occurred during the next two years, but in 1935 geology is grouped with physics under Professor A. L. McAulay, but with a note that a Lecturer in Geology (part-time) was to be appointed. No one appears to have been appointed in that year or the next. In 1938 the Department was still Physics and Geology, but no mention was made of an appointment in geology and no details for geology were published. In that year P. J. MacLeod resigned and was replaced by Ernst Edgar Kurth, D.Sc., who later became Professor of Chemistry.

Geology was apparently entirely dropped from 1938 to 1945, but in 1946 S. W. Carey was appointed the first Professor of Geology in the University of Tasmania, and early this year Maxwell Robert Banks, B.Sc., was appointed Lecturer. It is to be hoped that from now on the teaching of geology will be on a much more satisfactory footing than in the past.

Samuel Warren Carey graduated in the University of Sydney B.Sc. in 1933, M.Sc. in 1934 and D.Sc. in 1939. He was on active service during the second world war and soon after his demobilization he became Chief Geologist on the Tasmanian Geological Survey and from that position transferred in 1946 to the newly established Chair of Geology in the University of Tasmania.

QUEENSLAND.

The University of Queensland was opened in 1910. One of the early appointments was that of H. C. Richards, who was elected Lecturer-in-Charge of Geology in 1911.

Henry Caselli Richards was born at Melton, Victoria, in 1884, and received his early training in Geology at the University of Melbourne, where he graduated B.Sc. in 1907, M.Sc. in 1909 and D.Sc. in 1915.

He was the second holder of the Caroline Kay Scholarship in Geology and subsequently held a Government Research Scholarship, but resigned this Scholarship to become Lecturer-in-Charge, Chemistry and Mining Department of the Technical School, Brisbane, and held this post during 1910-11, and then resigned to accept the Lectureship in Geology at the newly established University of Queensland.

In 1919 the Chair of Geology was founded and Richards became the first Professor of Geology in the University of Queensland. He was still the holder of the Professorship at the time of his death this year. He has left behind him a long record of research ably accomplished. Richards has filled many important posts, such as President of the Professorial Board, 1925-31; Deputy Chancellor of the University of Queensland, 1946; Chairman of the Great Barrier Reef Committee since 1925, when he was instrumental in its establishment. He was also Chairman of the Queensland Committee of the C.S.I.R. from 1926.

Richards was President of Section C (Geology), A.A.A.S., in 1924 at the Adelaide meeting. In his presidential address he summarized and brought up to date our knowledge of the volcanic rocks of Queensland. He was also a member of the Executive of the Australian National Research Council from 1923 to 1932.

Richards was associated with Markham on a survey of Museums and Art Galleries in Australia under the auspices of the Carnegie Corporation of New York. The report was published in 1933 and as a result of certain recommendations the Art Galleries and Museums Association of Australia and New Zealand was formed and Richards was President in 1937. Richards was in charge of the teaching of geology at the University since its establishment and,

aided by very able assistants, has set a standard, as to administration, teaching and research which it will be difficult to find equalled in any other University of similar age and size.

In 1913 A. B. Walkom was appointed Lecturer in Geology at the University of Queensland.

Arthur Bache Walkom was born at Grafton, New South Wales, in 1889 and was educated at Fort St. School and the University of Sydney, where he graduated B.Sc. in 1910 and D.Sc. in 1918. He was Macleay Fellow of the Linnean Society of New South Wales during 1912-13 and then joined the staff of the Geological Department of the University of Queensland, but resigned in 1919 to accept the Secretaryship of the Linnean Society of New South Wales. He was appointed Director of the Australian Museum in 1940, a position which he still holds.

While in Queensland Walkom was Honorary Secretary of the Royal Society, 1916-18, and President, 1918-19. He also carried out extensive research on the fossil flora of Queensland, particularly that belonging to the Mesozoic period, and published numerous papers in the Royal Society of Queensland and elsewhere. In 1929 Walkom attended the British Association meeting in South Africa, and in 1930 was given six months' leave, and while holding a Rockefeller Foundation Scholarship spent some time studying palaeobotany under Seward. In 1933, at the invitation of the Geological Society of America, Walkom attended the Sixteenth International Geological Congress at Washington. He was Secretary of the Linnean Society from 1919 to 1940 and President 1941-42. He was President of the Royal Society of New South Wales 1943-44.

The A.N.Z.A.A.S., formerly the A.A.A.S., owes a debt of gratitude to Dr. Walkom for his long and able service as Honorary General Secretary from 1926 to 1947.

Dr. Walkom is the leading authority on fossil plants in Australia and has made the Mesozoic flora of Australia his special subject of research.

Walkom was succeeded as Lecturer in Geology by W. H. Bryan in 1920.

Walter Heyward Bryan was born at Brisbane in 1891. He was educated at Ipswich Grammar School and the Universities of Queensland and Cambridge. He graduated B.Sc. in 1914, M.Sc. in 1916 and D.Sc. in 1926. He joined the Geological Survey of Queensland in 1914 but resigned in 1915 to enlist in the A.I.F. for active service in World War I. He served in Gallipoli and France and was mentioned in despatches and awarded the M.C.

Soon after being demobilized, Bryan was appointed Lecturer in Geology at the University of Queensland. In 1946 the Council of the University of Queensland conferred the well-merited title of Associate Professor of Geology on Dr. Bryan.

Bryan was President of the Royal Society of Queensland in 1924. His research work has dealt with many branches of geology, perhaps more especially with palaeogeography, and his publications are numerous and of a uniformly high standard.

In 1926 the Geological Department had grown to such an extent that another senior member of staff became necessary, and F. W. Whitehouse was appointed Lecturer.

Frederick William Whitehouse was born at Ipswich in 1900 and was educated at the Ipswich Grammar School and the Universities of Queensland and Cambridge. He graduated B.Sc. in 1922 with First Class Honours and University Gold Medal. Whitehouse was awarded a Queensland University Foundation Travelling Scholarship, and this allowed him to enter Cambridge, where he won the Ph.D. degree. In 1926 he was appointed to the John Thomson Lecture-ship in Geology at the University of Queensland. Prior to the war he did extensive field work in north-western Queensland and central Australia. In

1941 he enlisted in the A.I.F. and served in New Guinea and northern Australia. He gained his commission in 1942. Whitehouse won the D.Sc. Queensland in 1939. He has been Honorary Palæontologist to the Queensland Museum and Palæontologist to the Geological Survey of Queensland. The main interest of Whitehouse has been in palæontology, and he has published many valuable papers on this subject, more particularly in respect to Cambrian and Cretaceous faunas, and has, in addition, published many other papers on general and structural geology.

In 1940 A. O. Jones was appointed Lecturer in Geology. Arthur Owen Jones graduated B.Sc. in the University of Queensland in 1925 and M.Sc. in 1927.

In 1946 Dorothy Hill was also appointed a Lecturer. Dorothy Hill graduated B.Sc. in 1928, M.Sc. in 1930, and D.Sc. in 1942. In addition Dr. Hill studied at Cambridge and won the Ph.D. of that University. During the second world war Dorothy Hill held a commission in the W.R.A.N.S. She is now one of our leading palæontologists and has specialized in the Corals and Bryozoa, and has published numerous papers, principally in the *Proceedings of the Royal Society of Queensland*.

Two other recent appointees are Edward Valentine Robertson, B.A., who was Demonstrator from 1941 to 1945, and was then appointed Temporary Lecturer, and Jack Tunstal Woods, who graduated B.Sc. in 1946 and has been Demonstrator in Geology in 1946-1947.

WESTERN AUSTRALIA.

The University of Western Australia was opened in 1912 and Geology was among the Foundation Chairs. The first Professor was Walter George Woolnough.

Woolnough was born in 1876 at Brushgrove, New South Wales, and was educated at Newington College and the University of Sydney, where he graduated B.Sc. in 1898 and D.Sc. in 1904, being the first person to be admitted to this degree at the University of Sydney.

After graduating, Woolnough was appointed Demonstrator in Geology in Sydney, but resigned in 1902 to become Lecturer in Geology and Mineralogy at the University of Adelaide. This post was established after the death of Professor Tate, when the work in geology was divided between W. Howchin and W. G. Woolnough, both with the title of Lecturer. Woolnough resigned from Adelaide in 1905 and returned to Sydney as Lecturer in Geology under Professor David. He was Acting Professor of Geology during David's absence with the Shackleton Antarctic Expedition, 1907-09. In 1911 Woolnough was made Assistant Professor of Geology in the University of Sydney, but transferred in the following year to Western Australia to become the first Professor of Geology in the newly established University of Western Australia. During World War I Woolnough began investigating salt deposits in Australia on behalf of the Brunner Mond Co. (now Imperial Chemical Industries). This work was of national importance and finally as the work necessitated so much travelling, etc., he felt obliged to resign his Chair. Woolnough remained with Brunner Mond until 1927, when he became Geological Adviser to the Commonwealth Government from 1927 till his retirement in 1941. During World War II his services were retained and he became Chief of Information Section, Directorate of Technical Practice, Ministry of Munitions, Melbourne.

In 1897 Woolnough was a member of David's party at Funafuti and he was the leader of expeditions to Fiji in 1901 and 1905. In all these undertakings valuable geological and geographical information was obtained. In 1911 the Commonwealth Government sent a scientific expedition to the Northern Territory and Woolnough was the chief geologist of the party. He was the Chairman of

the Royal Commission on the Collie Coal Industry, Western Australia, in 1914-15. During his time with Brunner Mond, Woolnough travelled over much of central Australia, especial attention being paid to salt lakes such as Lake Eyre.

As Geological Adviser to the Commonwealth, he had to report on oil, and was sent by the Government to study the oil areas of the United States. This was in 1930, and two years later Woolnough carried out the first aerial survey of the possibilities of oil in Australia.

At the Auckland meeting of the A.N.Z.A.A.S. in 1937 Woolnough was President of Section C (Geology), where he gave an address on Fact and Theories in Geology, with Special Reference to Petroleum, Salt and Coal. He was President of the Royal Society of New South Wales, 1926-27.

During the absence of Woolnough with Brunner Mond, Marcel Auroousseau, a graduate of Science of the University of Sydney, was appointed Lecturer-in-Charge and carried on after Woolnough's retirement until he left to join the Carnegie Geophysical Institute of Washington in 1920. During the latter portion of 1920, after Auroousseau's departure, Howard Bolitho Hauser, B.Sc., Melbourne, took over the work of the Department until the end of the year. The Council of the University decided not to make another appointment of a Professor, and in 1921 Edward de Courcy Clarke was appointed Lecturer-in-Charge of Geology.

Clarke was born in New Zealand in 1880, and was educated at the High School, Napier, New Zealand, and at University College, Auckland, where he graduated B.A. in 1901 and M.A. in 1902. After holding the position of Science Master at the Auckland Grammar School from 1901-05, Clarke joined the Geological Survey of New Zealand, but in 1910 returned to University College, Auckland, as Demonstrator in Geology, but soon left to join the Geological Survey of Western Australia. In 1921 he resigned from the Survey to become Lecturer in Geology at the University. The position was raised to the status of Associate Professor in 1926 and to Professor in 1930. Professor de Courcy Clarke has had charge of the Geological Department of the University of Western Australia for over twenty-six years, and although for a large portion of that time he had little if any assistance in running his Department, he has managed to do much research work and to publish many important papers dealing with the geology of Western Australia.

Clarke was President of Section C (Geology) of the A.N.Z.A.A.S. in 1930 at Brisbane, and gave an important address on the Pre-Cambrian rocks of Western Australia.

In 1934 Rex T. Prider was appointed Assistant Lecturer, and Lecturer in 1939.

Rex Prider graduated B.Sc. in 1932, and later at Cambridge won the Ph.D. in 1938. He was admitted to the degree of D.Sc. (Western Australia) in 1946.

At present R. W. Fairbridge is also Lecturer in Geology. He graduated B.Sc. at Oxford, B.A. Canada and D.Sc. Western Australia in 1944.

Dorothy Carroll, who graduated B.Sc. in 1922 and later Ph.D. London in 1936, has done excellent work on microscopic examination of soil particles and held a Research Fellowship from 1939.

Curt Teichert (see above under "Melbourne") also held a Research Fellowship for a period.

This brings the history of the Teachers of Geology in Australian Universities up to 1947, and covers a period of nearly one hundred years in the case of Melbourne with lesser periods in the case of other Universities.

While most of those who were appointed in the early days of geological education in Australia were from overseas, most of the later appointments to Professorships or Lectureships have been from Australian-

trained if not Australian-born graduates. Queensland is unique in that every person who holds or has held a senior post on the staff of the Geological Department of the University was born in Australia—Richards (Victoria), Walkom (New South Wales), Bryan, Whitehouse, Jones and Dorothy Hill (Queensland), and at the present time all members of staff are Queenslanders. It may be noted that at present Sydney has only Sydney graduates on the staff of its Geology School, and likewise Melbourne has only Melbourne graduates on its staff, except in the case of Dr. Teichert. There are two members of the teaching staff of the Department of Geology in Tasmania, and both are graduates of the same University—that of Sydney.

This concentration of graduates from a single University is probably not the wisest arrangement and would be truly dangerous but for the fact that young graduates are encouraged to go abroad to study at older Universities either with or without the idea of obtaining the Ph.D. degree. In this way their ideas and methods of teaching, research, etc., are widened and contacts with fellow workers in overseas Universities are established. Even then there has been the tendency for Sydney graduates to concentrate rather on Cambridge and Melbourne on the University of London.

To my mind it is certain that a round-table conference between the Professors of Geology in Australia to discuss questions of overseas study and future staffing would lead to a better and wider distribution of knowledge than occurs under the present system, and I would recommend the idea of such a conference to their serious consideration.

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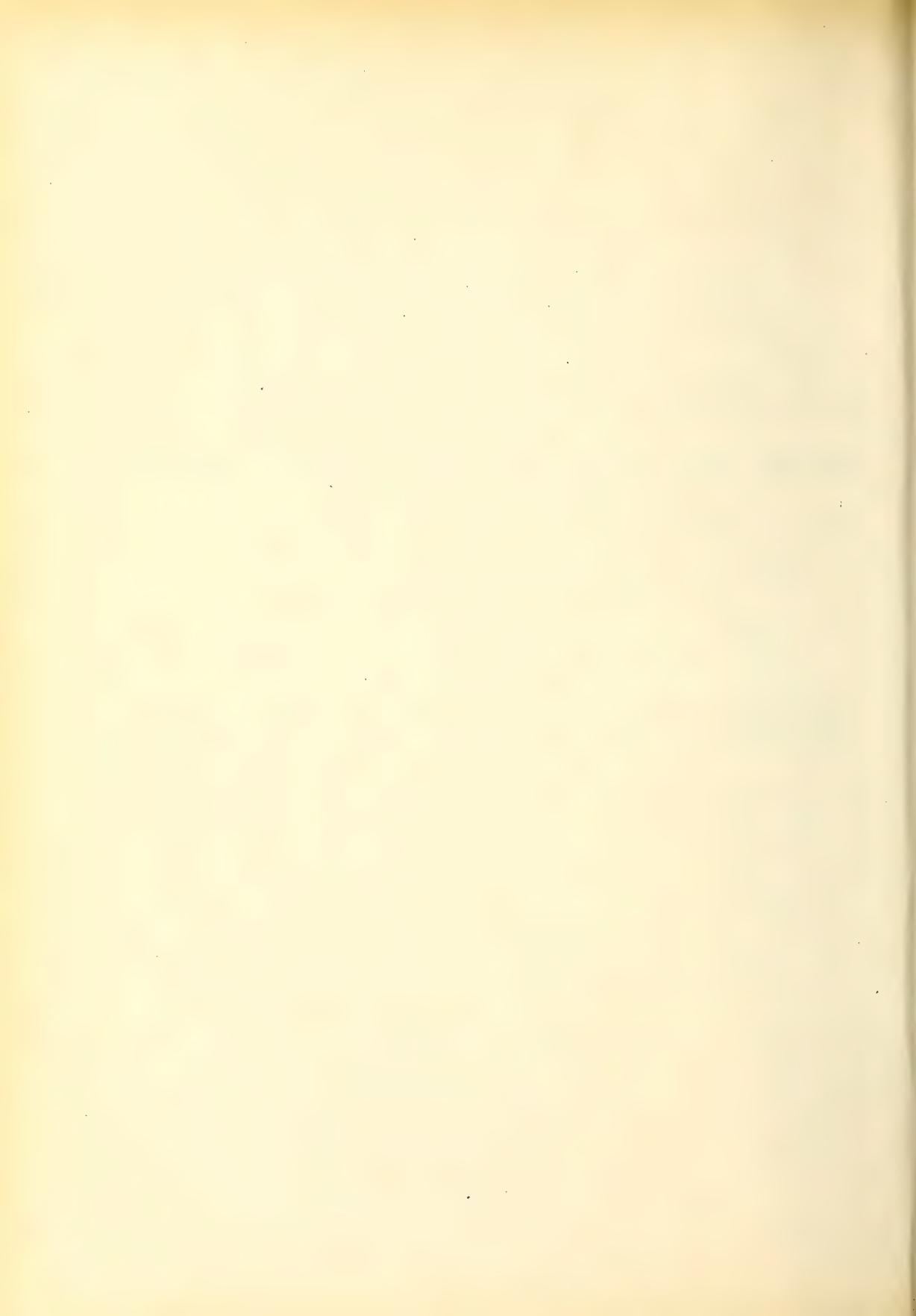
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PART III



THE COLORIMETRIC DETERMINATION OF IRON IN CANNED FOODS WITH 1, 10 PHENANTHROLINE.

By HUGH A. MCKENZIE, M.Sc.

Manuscript received, July 10, 1947. Read, August 6, 1947.

INTRODUCTION.

Investigations in this laboratory on the corrosion of tinfoil containers by foodstuffs frequently require trace iron determinations. While there is no lack of information in the literature on chromogenic agents for iron, comparatively few are well suited to the quantitative determination of small amounts of iron. (Sandell, 1944.)

The characteristics of the more common reagents have been examined by Woods and Mellon (1941), who concluded that the most generally suitable were 1, 10 phenanthroline (ortho-phenanthroline) and 2, 2' dipyridyl. Phenanthroline is colourless and reacts stoichiometrically with ferrous iron to form the intensely orange red coloured tris 1, 10 phenanthroline ferrous ion which is stable for long periods over the pH range 2 to 9. The complex ion obeys Beer's Law over a wide range of concentration. Phenanthroline is somewhat superior to dipyridyl as its complex is stable over a wider pH range and it is more readily available at a cheaper price. It will be seen later that it has the further advantage in the present application of being less subject to interference by citrate.

In the above corrosion experiments it is frequently necessary to determine iron in the presence of many times its amount of tin. Evidence was soon obtained which indicated that tin could interfere in the iron determination. It was therefore necessary to pay special attention to this interference.

A colorimetric method has been developed which involves wet digestion, use of p-hydroxy phenyl amino acetic acid (glycin) as reductant and 1, 10 phenanthroline as chromogenic agent.

BASIS OF THE METHOD.

Destruction of Organic Matter.

For reasons which have been adequately discussed by Piper (1942) wet digestion was chosen in preference to dry ashing for destruction of organic matter.

The Reduction.

The colour reaction with phenanthroline is given by ferrous but not by ferric iron. Since the iron is present as ferric sulphate after digestion it is necessary to reduce it to the ferrous state. A review of the literature indicates a rather confusing, and in some cases contradictory, mass of information on the use of reductants for trace iron determinations.

Saywell and Cunningham (1938) studied several reducing agents, including hydroxylamine hydrochloride, sodium hypophosphite and sodium formate; but finally used hydroxylamine on account of its freedom from iron. Hummel and Willard (1938) found sodium dithionite (hydrosulphite) unsatisfactory and employed hydroquinone with success. Fortune and Mellon (1938) found sodium sulphite, sodium formate and formaldehyde unsatisfactory and used

hydroxylamine hydrochloride. Dauphinee and Campbell (1937) found p-hydroxy phenyl amino acetic acid (the photographic, chemical glycin) to be suitable.

It will be seen later that it is necessary to carry out the colour reaction in the presence of sodium citrate. Cowling and Benne (1942) found that hydroxylamine hydrochloride was unsatisfactory under such conditions and used hydroquinone. The present author has found that in his procedure glycin is entirely satisfactory and superior to hydroquinone. Using glycin as reductant, maximum colour development for the maximum amount of iron determined took five minutes at 25° C., whereas at least 30 minutes were required with ten times as much hydroquinone.

Gerber *et al.* (1942) claim that glycin solution must be made up fresh each day. The present author has found that glycin solution (0·1 per cent. in 0·4 N sulphuric acid) stored for one month at 25° C. is still effective as reductant. It is of interest to note that both hydroquinone and glycin solutions must be prepared in acid solution for maximum stability.

The Colour Reaction : The Interference of Diverse Ions.

A critical examination of the influence of some fifty ions on the determination of iron with phenanthroline was made by Fortune and Mellon (1938). It was found difficult to make a general statement regarding the interference of an ion since the extent of interference frequently depended on the procedure followed.

Some attempt has been made to examine the effect of interfering ions on the determination in biological materials, but this work has been restricted to methods involving dry ashing.

The influence of certain elements which could possibly interfere in the determination and be present in canned foods in appreciable amounts was, therefore, examined.

(i) *Tin*. Known amounts of iron were determined in the presence of definite amounts of tin in synthetic solutions which had been subjected to the usual digestion. The method of determination was similar to that described in the recommended procedure, except that no sodium citrate was present. (Ammonium acetate was used as buffering agent.) There was no significant error in the determination of 25 microgrammes (γ) (5 p.p.m.)* of iron in the presence of 500 γ (100 p.p.m.) of tin but for 1,250 γ (250 p.p.m.) and 2,500 γ (500 p.p.m.) of tin the error was about -10 per cent. Even if the solutions were allowed to stand overnight there was no change in the interference.

The amounts of glycin and phenanthroline used were equivalent to 350 and 750 γ of iron respectively. With smaller amounts of glycin and phenanthroline the error was usually greater and could be as high as -20 per cent. Interference was sometimes observed in the presence of only 500 γ of tin, when half the amount of glycin and one-quarter the amount of phenanthroline were used. While excess of reductant and chromogenic agent did have some effect on the interference, it was not possible to eliminate it completely by this means.

It is well known that sodium citrate forms a very stable complex with both stannous and stannic tin. It was therefore decided to determine the effect of sodium citrate on the interference of tin in the iron determination. Citrates have actually been used by other workers in the determination of iron in biological materials (by phenanthroline). Cowling and Benne (1942) used small amounts of ammonium citrate to overcome the interference of aluminium phosphate in the determination. Bandemer and Schaible (1944) used sodium citrate for adjustment of the pH, in preference to acetate. They observed that the rate of colour formation was retarded by citrate.

* The figures in brackets are the original metal contents expressed as p.p.m. assuming the metal came from 5 g. of food.

Determinations carried out by the author on pure iron solutions using sodium citrate as buffering agent confirmed this effect. At 25° C. colour formation took at least 30 minutes to develop completely whereas at 12° C. several hours were required. Colour development at both temperatures using ammonium acetate was almost instantaneous.

A modified procedure was, therefore, tried involving a smaller amount of sodium citrate (1 ml. of N in 50 ml. solution) and using N ammonium acetate as buffering agent. In digests of pure iron solutions the colour for 25 γ of iron was completely developed within four minutes at both 25° C. and 12° C. The colour for 200 γ was developed within five minutes at 25° C. and 10 minutes at 12° C.

The determination of iron in the presence of tin was then repeated using the smaller amount of sodium citrate. The results are shown in Table 1. It is seen that there is no significant error introduced by the presence of as much as 2,500 γ of tin. The readings were taken after fifteen minutes, which is sufficient for maximum colour development.

It is of interest that the retardation effect of citrate was present when determinations were made on solutions of ferrous iron. At the pH of the reaction sodium citrate probably forms a strong complex with the iron (Lingane, 1946) from which the phenanthroline has some difficulty in removing the iron.

Sodium citrate exerts a greater retarding influence on the development of the colour with 2, 2' dipyridyl, making this reagent less suitable when the colour reaction is carried out in the presence of citrate. This greater effect for dipyridyl may be associated with the somewhat greater instability constant of its iron complex (Dwyer and Nyholm, 1946 ; Dwyer and McKenzie, 1947).

(ii) *Zinc*. Morgan and Rawlings (1943) have shown that it is unlikely that the zinc content of foods would exceed 100 p.p.m. Zinc can form a colourless complex with phenanthroline, but it is doubtful if it would interfere in these amounts with the large excess of phenanthroline which is used in the recommended procedure. This has been tested experimentally and the results in Table 1 show that the only appreciable interference is in the determination of 200 γ (40 p.p.m.) of iron in the presence of 2,500 γ (500 p.p.m.) of zinc. So that there is no interference by zinc in the amounts which might reasonably be present in canned foods.

(iii) *Copper*. According to Morgan and Rawlings (1943) the copper content of foods rarely exceeds 50 p.p.m., this figure probably only being reached by tomato products. Copper may form a weakly coloured complex with phenanthroline, and its extent of interference was therefore studied. The results in Table II show that even as much as 250 γ (50 p.p.m.) of copper produce no appreciable interference.

(iv) *Nickel*. It is doubtful if the nickel content of canned foods would exceed 5 p.p.m. Nickel forms a weakly coloured complex with phenanthroline. The results in Table I show that amounts of nickel up to 250 γ (50 p.p.m.) produce no significant interference.

(v) *Calcium*. Certain canned foods may have very high natural calcium contents, e.g. silver beet 6,000 p.p.m., whereas others may have high contents due to treatment with calcium chloride brines during processing, e.g. potatoes 2,000 p.p.m. The diluted digests of such foods always show appreciable precipitates of calcium sulphate. The possible interference by adsorption was therefore examined. The results in Table I show no appreciable interference.

(vi) *Phosphorus*. Pyrophosphate interferes badly in the determination of iron in methods involving dry ashing unless the ash solution is specially treated, but in wet digestion pyrophosphate is transformed to orthophosphate from which there is probably little interference. The results shown in Table I verify this.

TABLE I.
Influence of Diverse Elements on the Determination.

Micrograms of Iron per 50 ml.	Original Iron Content. p.p.m.	Added Element.	Micrograms of Added Element.	Original Content of Added Element. p.p.m.	Iron Content Found. p.p.m.	Error per Cent.
25	5	Tin	500	100	4.8	-4
25	5	"	500	100	4.9	-2
25	5	"	500	100	5.0	0
25	5	"	500	100	5.0	0
25	5	"	1,250	250	4.9	-2
25	5	"	1,250	250	5.1	+2
25	5	"	1,250	250	5.0	0
25	5	"	1,250	250	5.0	0
25	5	"	2,500	500	5.1	+2
25	5	"	2,500	500	5.0	0
25	5	"	2,500	500	5.1	+2
25	5	"	2,500	500	5.2	+4
25	5	Zinc	500	100	5.0	0
200	40	"	500	100	40.0	0
25	5	"	1,000	200	4.9	-2
200	40	"	1,000	200	40.0	0
25	5	"	2,000	400	4.9	-2
200	40	"	2,000	400	39.5	-1
25	5	"	2,500	500	5.0	0
200	40	"	2,500	500	36.8	-8
25	5	Copper	100	20	5.0	0
25	5	"	100	20	4.9	-2
25	5	"	250	50	5.0	0
25	5	"	250	50	4.9	-2
25	5	Nickel	100	20	5.0	0
25	5	"	100	20	5.0	0
25	5	"	250	50	4.9	-2
25	5	"	250	50	4.9	-2
10	2	Calcium	25,000	5,000	2.0	0
25	5	"	25,000	5,000	5.0	0
50	10	"	25,000	5,000	9.9	-1
25	5	"	50,000	10,000	4.9	-2
25	5	"	50,000	10,000	4.9	-2
25	5	Phosphorus	20,000	4,000	4.9	-2
25	5	"	20,000	4,000	5.0	0
25	5	Aluminium phosphorus	500	100	4.9	-2
			2,500	500		
25	5	Aluminium phosphorus	2,500	500	5.1	+2
			2,500	500		
25	5	Aluminium phosphorus	2,500	500	4.9	-2
			2,500	500		

Note.—The amounts of iron and added element are expressed as micrograms present in 50 mls. of solution. They are also expressed as p.p.m. assuming this amount of element came from 5 g. of food.

(vii) *Aluminium.* Cowling and Benne (1942) found that aluminium and phosphate interfered in the determination of iron, if the ratio of aluminium to iron were greater than two to one, by co-precipitation of iron with aluminium phosphate, unless citrate was present. The extent of aluminium phosphate interference was examined in the present work and as can be seen from Table I is negligible. With the higher amount of aluminium (500 p.p.m.) and phosphorus (500 p.p.m.) a precipitate occasionally occurred at the end of the digestion

TABLE II.
Recovery Tests in Canned Foods.

Food.	Iron Content.				$100 \frac{b}{a}$
	Initial p.p.m.	Added p.p.m.	Calculated (a) p.p.m.	Found (b) p.p.m.	
Orange juice	3.0	2.0	5.0	5.0	100
	5.1	10.0	15.1	14.8	98
	2.3	5.0	7.3	7.2	99
	3.5	20.0	23.5	23.4	100
Potatoes	5.8	2.0	7.8	8.6	110
	5.8	5.0	10.8	10.8	100
	5.0	5.0	10.0	9.8	98
	5.0	20.0	25.0	25.1	100
Beetroot	3.4	5.0	8.4	8.4	100
	7.2	10.0	17.2	17.5	102
Silver beet	16.4	10.0	26.4	26.8	102
	17.7	10.0	27.7	28.0	101
Cabbage	15.4	5.0	20.4	20.1	98
	23.5	5.0	28.5	28.9	101
	14.9	10.0	24.9	25.1	101
Peaches	3.0	10.0	13.0	12.9	99
Asparagus	4.1	10.0	14.1	14.3	102
Tomatoes	10.0	10.0	20.0	20.6	103
	10.0	20.0	30.0	30.3	101
Beans	12.4	10.0	22.4	23.1	103
	9.2	10.0	19.2	19.2	100

which subsequently interfered, but if the diluted digest were boiled this precipitate dissolved. It is extremely unlikely, however, that the aluminium content would exceed 100 p.p.m.

Measurement of the Colour.

The absorption curve for the tris 1, 10 phenanthroline ferrous ion shows a maximum at 508 m μ with a secondary maximum at 474 m μ . On the Evelyn photoelectric colorimeter maximum absorption is given by the 490 and 470 m μ filters. Beer's Law is obeyed for the 490 filter only over the range 10 to 100 γ (per 50 mls.) of iron, but for the 470 filter over the whole working range 10 to 200 γ of iron, and the latter has, therefore, been used for the colour measurement.

RECOMMENDED PROCEDURE.

Reagents.

- Water: Distilled water, redistilled from Pyrex.
- Nitric Acid: 16 N. A.R. (Redistilled if necessary.)
- Sulphuric acid: 36 N. A.R. (Redistilled if necessary.)
- Hydrogen peroxide: 30 per cent. (100 volume). B.P.
- Sodium citrate: 25 g. dissolved in 100 mls. of water.
- P-hydroxy phenyl amino acetic acid.
- Photographic glycin: 0.1 g. dissolved in 100 mls. of 0.4 N sulphuric acid.
- 1, 10 phenanthroline: 0.4 gm. dissolved in 100 mls. of 2 per cent. acetic acid.
- Ammonium hydroxide: Concentrated A.R. redistilled from Pyrex.
- Ammonium acetate: A.R. 70 g. dissolved in 1 litre of water.

Apparatus.

A spectrophotometer or photoelectric colorimeter.

(An Evelyn photoelectric colorimeter manufactured by the Rubicon Co., Philadelphia, U.S.A., was used by the author.)

The water was redistilled in the apparatus described by Piper and Oertel (1941).

Method.

Mix the sample of food with nitric acid (20 mls.) and sulphuric acid (10 mls.) in a Kjeldahl flask (500 mls.).

(*Note.*—50 g. samples are usually taken, representative sampling being obtained by homogenization in the Waring Blendor. This sample size is used because determinations of several metals are made on the final digest.)

The digestion procedure, involving the use of hydrogen peroxide, has been described in detail by McKenzie (1945). Make up the digest to 50 mls. Transfer a 5 ml. aliquot, preferably containing 20 to 200 γ of iron, to a 50 ml. volumetric flask. To this add sodium citrate solution (1 ml.), glycin solution (1 ml.) and phenanthroline (2 ml.).

From a burette add the amount of ammonium hydroxide required to give a pH of approximately 3.8. Make up to volume (50 mls.) with ammonium acetate. Remove any precipitate by centrifuging. Allow to stand for 15 minutes after making up to volume. Read the transmittance on the photoelectric colorimeter (470 m μ filter for the Evelyn colorimeter) or spectrophotometer.

Recovery Tests.

Satisfactory evidence for the validity of the method is given by the recovery tests in pure solutions described above. Recovery tests in canned foods provide useful confirmatory evidence, although this is somewhat circumstantial particularly when the initial iron content is high.

Typical recovery tests are shown in Table II. The precision and reproducibility of the method are seen to be of the order of ± 3 per cent.

The following advantages are claimed for the method: (a) The method of wet digestion is very simple and safe; (b) there is no significant interference from insoluble matter; (c) the procedure is highly specific and not subject to interference from elements which might be present in canned foods, tedious separations being thereby eliminated; (d) the pH need not be accurately controlled; (e) the time for a determination is short.

SUMMARY.

A rapid, highly specific, method is described for the determination of iron in canned foods, using a wet digestion procedure, and a colorimetric determination with 1, 10 phenanthroline as chromogenic agent and p-hydroxy phenyl amino acetic acid (glycin) as reductant. It is shown that sodium citrate must be present to overcome interference by tin, and that in the presence of citrate glycin is the most satisfactory reductant. Dipyrldyl is unsuitable as chromogenic agent when citrate is present.

Recovery tests on pure solutions in the presence of various added elements and on canned foods show that the precision and reproducibility of the method are of the order of ± 3 per cent.

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The author is indebted to Miss H. Smith for her assistance during this investigation and also to Mr. E. Thompson and Miss A. White for synthesis of samples of phenanthroline.

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Food Preservation Research Laboratory,
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Homebush.

THE REACTION OF PYRIDINE WITH DICHLOROTETRAMMINE COBALT (III) COMPLEXES.

By J. A. FRIEND, B.Sc.,
and D. P. MELLOR, D.Sc.

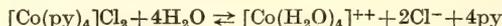
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In the course of an investigation of the polarographic behaviour of ammonia and ethylenediamine complexes of cobalt (III) (Willis, Friend and Mellor, 1945) an attempt was made to prepare the penta- and hexa-pyridine salts of the metal by heating trans-dichloro-tetrapyridine cobalt (III) chloride with excess of pyridine. Although the attempt was unsuccessful, it was thought that the reaction which did occur was of some interest since it involved the reduction of cobalt III to cobalt II. This reduction was unexpected because covalent octahedral complexes of cobalt III are usually stable as compared with those of cobalt II. For comparison, the reaction of pyridine with a number of other dichlorotetrammine cobalt III salts was also studied.

EXPERIMENTAL.

Reaction of Pyridine with Trans-dichlorotetrapyridine Cobalt (III) Chloride.

A small quantity (3.0 g.) of trans $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$, prepared by the method of Werner and Fenster (1906), was dissolved in 40 ml. of redistilled pyridine to give a green solution. This was evaporated on a water-bath until much of the pyridine had been driven off. During this process chlorine was evolved and could be detected by means of starch-potassium iodide. On cooling the solution, rose-pink crystals separated. Recrystallized from pyridine, in which they dissolved to give a blue solution, the pink crystals separated once more. The compound could be kept indefinitely in a stoppered tube but in the air it slowly turned blue. Analysis of the compound gave the following figures: Co, 13.4%; Cl, 15.4%. This suggested that the substance was $[\text{Co}(\text{py})_4]\text{Cl}_2$ (Co, 13.2%; Cl, 15.9%), a conclusion supported by molecular conductivity measurements on aqueous solutions. The value of μ_0 , $250\omega^{-1}$, indicated dissociation into three ions, most likely as follows:



Evidence for the existence of this type of reaction is to be found in an earlier paper (Willis *et al.*, 1945).

That reduction had occurred during the reaction between trans-dichlorotetrapyridine cobalt (III) chloride and pyridine was confirmed by means of polarographic and magnetic measurements.

On polarographic examination, the compound ($[\text{CoPy}_4]\text{Cl}_2$) was found to give a single step in 0.05 M K_2SO_4 with $E_{\frac{1}{2}} = -1.185$ volts corresponding to a reduction from Co^{II} to Co° (Willis *et al.*, 1945).

The magnetic susceptibility of the compound was found to be $+21.2 \times 10^{-6}$ c.g.s. units. If it is assumed that its formula is $[\text{Co}(\text{Py})_4]\text{Cl}_2$, this gives a value of 9450×10^{-6} c.g.s. units for ψ_M at 21° C.; correcting for diamagnetism gives a value of 4.85 Bohr magnetons for μ , a value well within the range found for ionic cobalt II complexes or complexes with sp^3 bonds (Mellor and Goldacre, 1940).

The Reaction of Pyridine with Dichloro-bis-ethylenediamine Cobalt (III) Chloride.

On refluxing trans (green) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ with pyridine it did not dissolve but at first slowly turned dark purple (owing to conversion to the cis compound) and finally red. The cis compound

itself, when refluxed with pyridine, also turned red without dissolving. The red compound was identified, by its cobalt content, as $[\text{Co}(\text{en})_2\text{pyCl}]\text{Cl}_2$ (Co required by this formula, 15.0% ; found, 15.6%).

The conversion was practically quantitative. There was evidence that traces of $[\text{Co}(\text{Py})_4]\text{Cl}_2$ were formed but undoubtedly the main reaction was the formation of the pentammine salt.

The Reaction of Pyridine with Dichlorotetrammine Cobalt (III) Chloride.

When *trans* $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is heated with pyridine it dissolves very slowly to give a green solution. At the end of two hours most of the original solid remained ; on filtering and evaporating the filtrate $[\text{Co}(\text{py})_4]\text{Cl}_2$ separated out, indicating that partial reduction had occurred. On the other hand no reduction occurs if *trans* $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is treated with concentrated ammonia solution. Instead, the chloropentammine salt is readily formed (Werner, 1911).

DISCUSSION.

Although there is no doubt that the product of the interaction between $[\text{CoPy}_4\text{Cl}_2]\text{Cl}$ and pyridine is a cobaltous compound, it does not necessarily follow that pyridine acts directly as a reducing agent¹ in the ordinary sense of that term. The following mechanism may account for the reaction. The first step consists of the formation of an unstable complex, $[\text{CoPy}_5\text{Cl}]^{++}$ or $[\text{CoPy}_6]^{+++}$, whose oxidation-reduction potential is greater than 1.35 volts, the value of the oxidation-reduction potential of chlorine. The unstable complex then oxidizes chloride ion to chlorine and *is itself reduced to the cobalt II stage*. Among hexammine cobaltic ions,² ability to oxidize chlorine ion appears to be confined to the unstable $[\text{Co}(\text{py})_6]^{+++}$ and $[\text{Co}(\text{py})_2(\text{NH}_3)_4]^{+++}$. It is not shown by $[\text{Co}(\text{en})_3]^{+++}$, $[\text{Co}(\text{en})_2\text{pyCl}]$ or $[\text{Co}(\text{NH}_3)_6]^{++}$.

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Werner, A., 1911. *Berichte*, **44**, 1887.
Werner, A., and Fenstra, 1906. *Ibid.*, **39**, 154.
Willis, J. B., Friend, A., and Mellor, D. P., 1945. *J. Am. Chem. Soc.*, **67**, 1067.

¹ It is of interest to note the difference in behaviour of Co^{III} and Rh^{III} . The pentapyridine and hexapyridine complexes of Rh^{III} can be readily prepared. Private communication from Dr. F. P. J. Dwyer.

² Another instance of the apparent reducing action of pyridine is to be found in the chemistry of ruthenium. If $\text{K}_2[\text{RuCl}_5\text{H}_2\text{O}]$ is treated with excess pyridine, orange needles of the composition $[\text{Ru}(\text{Py})_4\text{Cl}_2]$ separate. The change in valency of the ruthenium can be followed by means of magnetic susceptibility measurements. The moment of Ru^{III} in the first compound is 2.05 Bohr magnetons ; that of the Ru^{II} in the second is zero. (Unpublished experiments with Miss A. H. Cameron.)

A NEW METHOD FOR THE COMPARISON OF THE THERMAL CONDUCTIVITIES OF FLUIDS.

PART I.

By R. C. L. BOSWORTH, Ph.D., D.Sc.

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INTRODUCTION.

On account of the ease with which temperature differences in a fluid set up a system of convection currents the measurement of the thermal conductivity of a fluid has always been a singularly difficult problem in experimental physics, and, in consequence, reliable data for this property is relatively scarce. This is unfortunate in that the formulæ which have been developed for the treatment of the heat losses from various bodies in air, water or other fluids all involve the thermal conductivity of the fluid concerned. The magnitude of the thermal conductivity enters into such dimensionless parameters as the Peclet, Grashof, Prandtl and Nusselt numbers—all important in the treatment of thermal convection by the method of dimensions—and other more complicated quantities of a like nature, such as those concerned with the condensation of vapours. All this means that for many regular shaped bodies immersed in a given fluid we may calculate the convective heat loss to be expected if we know the thermal conductivity of the fluid concerned. It would seem reasonable therefore to attempt to reverse this process and calculate the thermal conductivity from measurement of the convective heat loss from bodies of known regular form immersed in the fluid.

Data on the heat loss from horizontal cylinders immersed in fluids are particularly well known and have been correlated by a relation between the Nusselt and the product of the Grashof and Prandtl numbers, viz. :

$$\frac{qd}{k\theta} = f\left(\frac{d^3\rho^2cg\beta\theta}{\eta k}\right) = f(ad^3\theta) \dots\dots\dots (1)$$

where

- q is the heat flow per unit area per unit time from the heated surface.
- d is the diameter of the heated cylinder.
- k is the thermal conductivity of the fluid.
- ρ is the density of the fluid.
- β is the coefficient of thermal expansion of the fluid.
- c is the specific heat (at constant pressure) of the fluid.
- η is the viscosity of the fluid.
- θ is the temperature difference between heated surface and bulk fluid.
- g is the local value of the gravitational field

and f(x) is an empirical function.

The composite property *a* is known as the convective modulus of the fluid. This property is related to other properties by

$$a = \frac{\rho^2cg\beta}{\eta k} \dots\dots\dots (2)$$

From an analysis of data collected by McAdams (1941) the author (Bosworth, 1944) showed that the function $f(x)$ could, within the accuracy of the experimental data, be put in the form

$$f(x) = 0.40 + 0.44x^{1/6} + 0.12x^{1/3} \dots\dots\dots (3)$$

and suggested that the thermal conductivity of a liquid could be obtained from measured data on convective heat loss by plotting $f^{\frac{1}{2}}$ against $x^{1/6}$. The paper further suggested that a resistance wire with a fine thermocouple welded to the central portion could be used as the heated cylinder. The power consumed is proportional to the square of the heating current (I) and the temperature difference (θ) to the reading of the thermocouple. Accordingly equation (3) suggests that $I/\theta^{\frac{1}{2}}$ should be plotted against $\theta^{1/6}$, and the intercept of the resultant line taken as proportional to the root of the thermal conductivity while the slope is proportional to the sixth root of the convection modulus of the liquid concerned. By this means it was suggested that the thermal conductivities and convective moduli of all fluids not being electrical conductors could be determined in terms of the properties of some standard fluid.

The mode of operation as suggested in the earlier paper has one serious practical objection. In order that the extrapolation to zero θ should be reasonably accurate the range of values of θ for which measurements are obtained should be very extensive, a range of 4^6 or 4,000 to 1 being desirable. There is an upper limit to the useful range of θ set by the boiling point of the liquid. For many liquids the upper limit may be taken as about 40° C., with still lower values for the more volatile liquids and possibly higher values for liquids of high boiling points. In order to get the desired range it would then be necessary that the lower value of θ should be 0.01° C. While a copper-constantan thermocouple and a laboratory galvanometer will detect a temperature difference of this order it is doubtful whether measurements of I^2/θ of the required accuracy could be obtained at such low values of θ , especially in view of the fact that a heated wire in a fluid shows transient phenomena (Bosworth, 1946) which appear to be of the longer time scale the lower the temperature difference. Accordingly it is considered that 0.1° C. is about the lowest value of θ for which measurements of I^2/θ at the required accuracy can be obtained. The requisite range of θ for the 1/6th power plot is therefore only attainable with the liquids of highest boiling point, and some other form of plotting is desirable in experimental work. For example it may readily be seen that equation (3), which after all is empirical and therefore approximate only, would give a straight line if $f(x)$ were plotted against $x^{1/3}$ provided x is not too small. Over a limited range of x we may always expand $f(x)$ in a Taylor series in powers of x or of \sqrt{x} . Let us write equation (3) in a more general form

$$\frac{qd}{k\theta} = \text{Const.} + f(ad^3\theta) \dots\dots\dots (4)$$

which postulates a physical condition in which the heat flow (per unit area per unit time) could be divided into two parts: one directly proportional to the temperature difference and to the thermal conductivity and the other proportional to a power of the temperature difference greater than the first and involving also the convective modulus as well as the thermal conductivity of the fluid.

THE EFFECT OF VARYING THE ORIENTATION OF THE HEATED SURFACE.

Any attempt to generalize equation (4) beyond the condition of applying to horizontal cylinders would suggest that if q/θ for any given hot body in a given fluid is plotted against θ , or any convenient function of θ , then the intercept will depend only on the geometry of the body concerned and the thermal conductivity of the fluid in which it is immersed. The slope, measured at some convenient point, will be a measure of the convective modulus of the fluid. As a first

Figure 1 shows q/θ versus θ data taken from a heated cylinder consisting of a length of nichrome wire 2.7 cms. long and 0.0315 cm. diameter immersed in distilled water at 26.2° C. and heated by an electric current which was increased steadily from 0.2 to 3.5 amps. for each orientation. The temperature excess (θ) was measured by means of a fine tungsten-nickel thermocouple welded to the centre of the resistance wire. The various I^2/θ versus θ curves shown in Figure 1 refer to orientations (α) of 0°, 43°, 57°, 73° and 90° measured from the horizontal. It appears clear from Figure 1 that the curves, although showing very different "slopes", all have, within experimental error, a common intercept on the I^2/θ axis. The "slopes" are the steeper the more nearly horizontal the wires. The relative "slopes" have been measured by measuring the relative ordinates (in excess of the intercept) at a number of different abscissæ and averaging. The "slopes" compared with the cosines of the angles (α) of inclination to the horizontal are given in Table I. It appears therefore that the magnitude of the convective heat loss is roughly proportional to the horizontal projected area.

TABLE I.

Variation of Convective Heat Loss in Distilled Water with Inclination (α) to the Horizontal.

"Slope" of the I^2/θ v. θ Curves Relative to Horizontal Wire.	Cos α .
1.00	1.00
0.67	0.73
0.47	0.54
0.30	0.29
0.05	0.00

A further series of experiments were carried out on the same wire immersed in a 92.2% solution of glycerol in water at 23° C. Glycerol has about half the thermal conductivity of water but a very much lower convective modulus—mainly on account of the high viscosity. The curves shown in Figure 2 refer to measurements at inclinations of 0°, 45°, 56°, 80° and 90° to the horizontal. The curves are very much less steep than the corresponding curves for water; but again it will be observed that the curves all give a common intercept on the I^2/θ axis, which may therefore be taken as a measure of the thermal conductivity of glycerine. The slopes, measured in the same way as above, are given in Table II.

TABLE II.

Variation of the Convective Heat Loss in Glycerine with Inclination (α) to the Horizontal.

"Slope" of the I^2/θ v. θ Curves Relative to that of Horizontal Wire.	Cos α .
1.00	1.00
0.68	0.71
0.52	0.56
0.14	0.17
0.08	0.00

The difference in the rate of convective heat losses from horizontal and vertical cylinders, apparent from the results of a number of observers, has been the object of comment by Carne (1937), who points out, in particular, that the variation of heat loss with diameter shows the same form in the two cases.

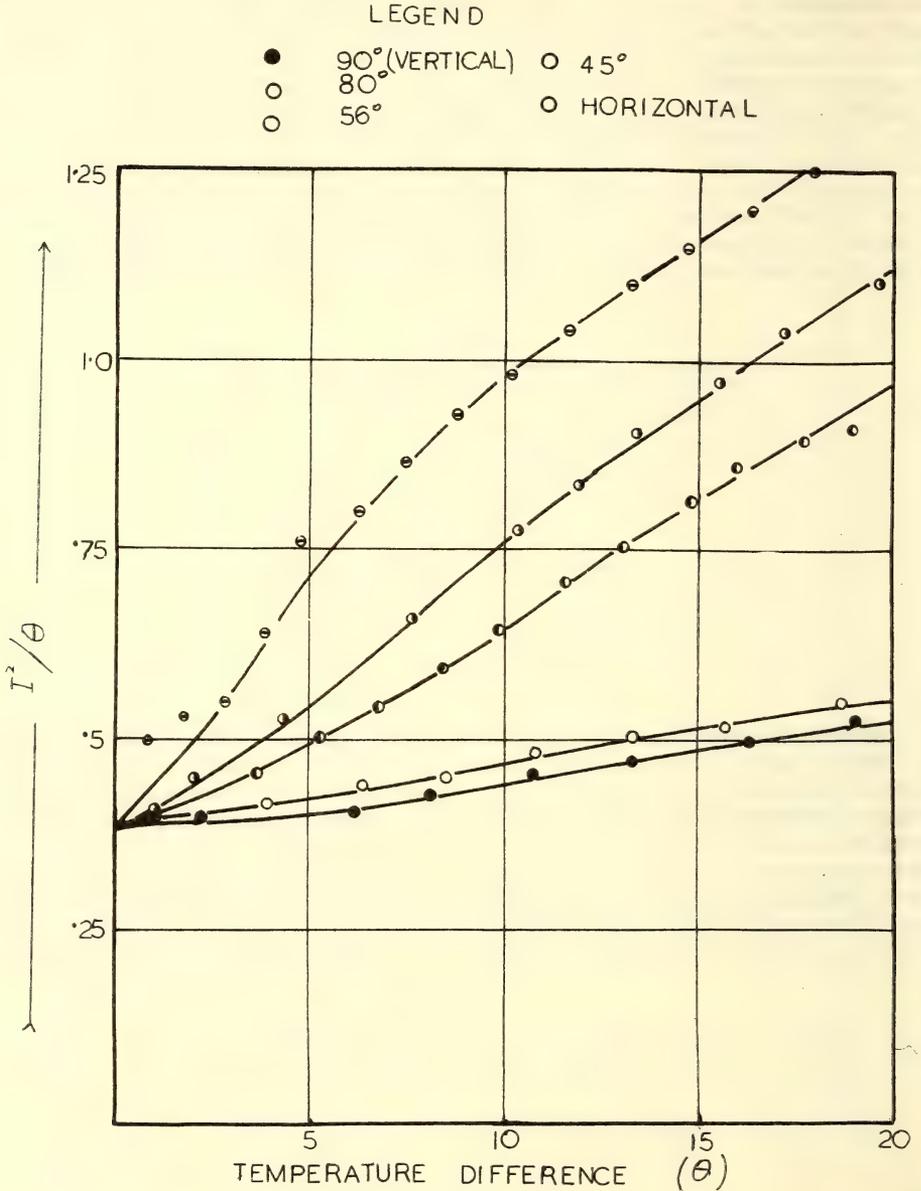


Fig. 2.

Figures 1 and 2 may be used to extend this observation. The curves for the heat losses at different orientations all have the same shape. The relationships between the rate of heat loss and the product of the Grashof and Prandtl numbers, applying to heated cylinders at different orientations, can be represented by functions of the same type differing only in the magnitude of the constants.

THE COMPARISON OF THE THERMAL CONDUCTIVITIES OF VARIOUS FLUIDS.

The equipment used for comparing the thermal conductivities of different fluids consisted of a single heated wire 4.5 cms. in length of 19 B & S gauge nichrome IV wire having a resistance of 0.074 ohm. To the centre of this there was welded a 34 gauge copper-constantan thermocouple. The resistance wire,

LEGEND

- | | |
|---------------------|------------------------|
| ○ WATER | • ETHYLENE GLYCOL |
| ◐ METHANOL | ● 92% GLYCEROL |
| ◑ 96% ETHYL ALCOHOL | ⊕ CARBON TETRACHLORIDE |
| ◒ ACETONE | ⊗ CHLOROFORM |
| ◓ ETHYL ACETATE | + FORMIC ACID |

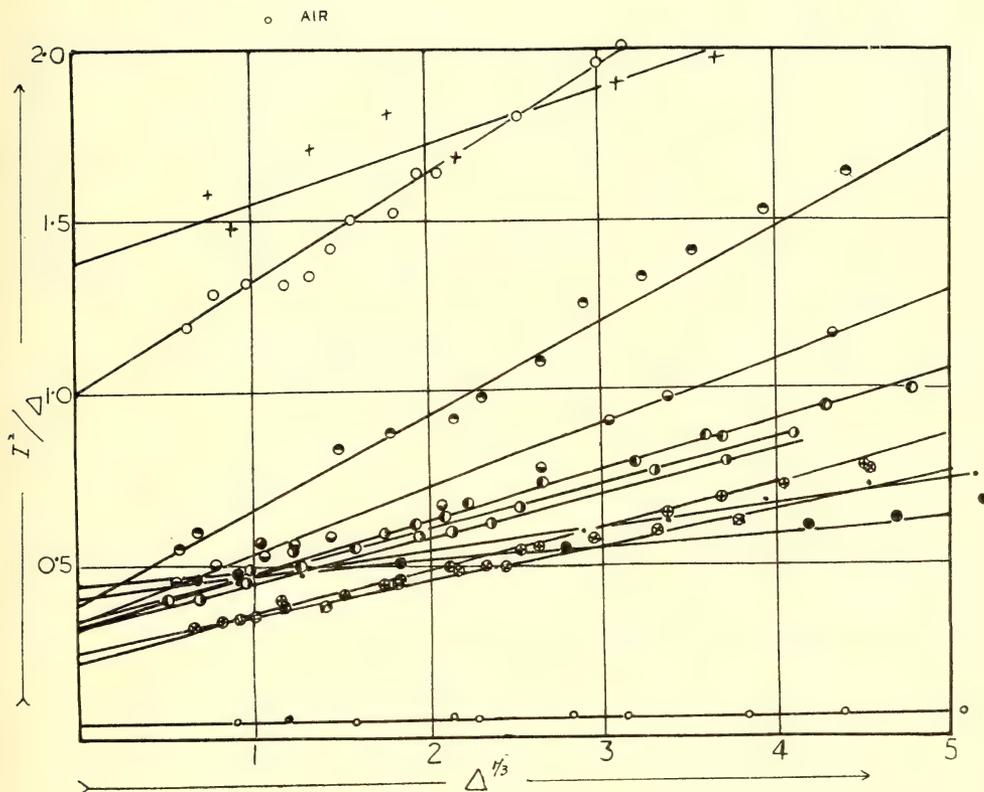


Fig. 3.

immersed in the fluid under test, was heated by A.C., the current being varied in the range from 0.2 to 20 amps. The lower limit with any given fluid being set by that giving the minimum measurable temperature rise as detected by the thermocouple, and the upper limit, in the case of a liquid, by that which just fails to produce boiling on the wire. The thermocouple was connected through a suitable shunt to a Cambridge Spot galvanometer, one division on the scale of which corresponded to a temperature rise of 0.336°C .

The first liquid to be examined was distilled water at room temperature (27°C). Readings were taken of the current (I) versus galvanometer reading

(Δ) (proportional to the temperature rise θ). Then were examined in order : toluene, benzene, acetic anhydride, 95% acetic acid, formic acid, a check reading on water, methanol, 92% glycerine, 96% ethyl alcohol, ethyl acetate, carbon tetrachloride, air, water, ethylene glycol, acetone, chloroform and carbon disulphide. In these experiments duplicate runs were quite satisfactory.

LEGEND

- ACETIC ACID ● ACETIC ANHYDRIDE
- ⊙ BENZENE ⊕ CARBON BISULPHIDE
- ⦿ TOLUENE ○ WATER

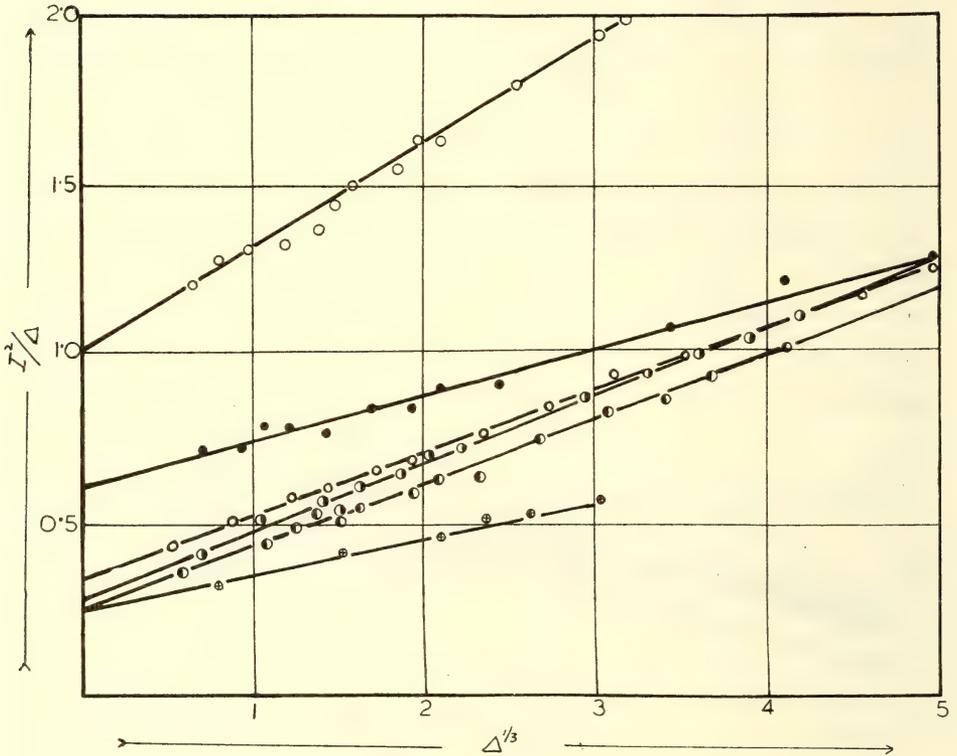


Fig. 4.

In the list of fluids above the one with the lowest thermal conductivity was the only gas examined—air. Any necessary correction for heat loss by radiation would therefore be most serious in this case. The value of the convective heat transmittance $h = q/\theta$ will be at its lowest at the lowest value of θ . The minimum value h_0 of h is by equation (3)

$$\frac{h_0 d}{k} = 0.40 \dots\dots\dots (5)$$

or $h_0 = 4k$

since $d = 0.1$ cm.

Since the thermal conductivity of air at 300° K. is 5.8×10^{-5} Cals. cms.⁻¹ sec.⁻¹ ° C.⁻¹, the lowest value of the convective transmittance with which we will be concerned will be 23×10^{-5} Cals. cms.⁻² sec.⁻¹ ° C.⁻¹. Radiative transmittance is given by

$$h_r = 4\epsilon\sigma T^3$$

where ϵ is the emissivity and σ the Stefan-Boltzmann constant. For the emissivity of bright nichrome at 300° K. we take a value 0.08 (the average of metals similar to nichrome as regards to spectral emittance as given by Amer. Inst. Phys. (1941)). The radiative heat transmittance is thus computed to be

$$h_r = 1.2 \times 10^{-5} \text{ Cals. cms.}^{-2} \text{ sec.}^{-1} \text{ }^\circ \text{C.}^{-1}$$

and accordingly the radiative heat loss amounts to only 5% of the convective in the case of air and is a still smaller fraction in all the liquid media. We are justified therefore in ignoring radiative heat loss in these experiments.

From the experimental data obtained as outlined above the values of I^2/Δ (proportional to q/θ) were given as a function of Δ (proportional to θ). A suitable form for presenting the data, as indicated by equation (3) above would be a plot of I^2/Δ versus $\Delta^{1/3}$. The experimental data presented in this way are given in Figures 3 and 4 in which the attached legends indicate the fluids to which the points refer. It will be noted that the points fall on straight lines, each giving a positive intercept on the I^2/Δ axis. The intercepts for each fluid studied measured relative to water at 27° C. are given in Table III.

TABLE III.

Relative Intercepts of the I^2/Δ versus $\Delta^{1/3}$ Lines.

Substance.	Relative Intercept.	Relative Thermal Conductivity.
Water	1.00	1.00
96% Ethyl alcohol	0.31	0.30
Ethylene glycol	0.42	0.44
92% Glycerine	0.47	0.48
Methanol	0.36	0.35
Formic acid	1.28	—
Acetic acid 95%	0.34	0.29
Acetic anhydride	0.61	—
Acetone	0.29	0.30
Ethyl acetate	0.28	0.28
Benzene	0.28	0.26
Toluene	0.25	0.24
Carbon tetrachloride	0.21	0.28
Chloroform	0.25	0.23
Carbon bisulphide	0.25	0.26
Air	0.041	0.040

Data for the relative thermal conductivities were obtained from the International Tables, the appendix of McAdams (1941) and from Keyes and Deem (1942). It will be observed from Table III that there is, in general, excellent agreement between the figures obtained by the present method and those which earlier had been accepted as representing the best available from the well-established methods.

Three possible sources of trouble became apparent during the measurements which led to these results. (1) Too high an electrical conductivity in the liquid under test will result in error due to a short-circuiting of the thermocouple e.m.f.

A high electrical conductivity would therefore lead to a spuriously high figure for the thermal conductivity as measured by this method. The high figure recorded in Table III for the thermal conductivity of formic acid may therefore be false. (2) When very volatile liquids (such as acetone or chloroform) were under test difficulty was experienced in obtaining a reproducible zero due apparently to a chilling of the cold junction of the thermocouple by surface evaporation of the liquid. All trouble of this nature could be eliminated by proper screening from convection currents in the air, or, better, by total enclosure. (3) In the very viscous liquids (such as glycerine), the time taken for the thermocouple to attain equilibrium was greatly prolonged. In the more limpid liquids a steady reading was attained in 1 to 2 minutes after switching on the current. In glycerine, particularly at low heating currents, times of the order 30 to 60 minutes were necessary. At higher heating rates the temperature of the wire in glycerine settled down to a steady value more rapidly.

ESTIMATION OF RELATIVE CONVECTIVE MODULI.

The experimental results as shown in Figures 3 and 4 can also be used to give a measure of the convective moduli of the fluids concerned. These figures may be interpreted by postulating that the heat loss factor can be represented by an equation of the type

$$\frac{qd}{k\theta} = A + B(ad^3\theta)^{1/3} \dots\dots\dots (6)$$

where A and B may be taken as constants over the range of θ for which data are available. For a given hot wire d is also a constant and we have

$$q/\theta = A'k + B'k(a\theta)^{1/3} \dots\dots\dots (7)$$

The intercepts from the lines obtained by plotting q/θ versus $\theta^{1/3}$ are therefore

$A'k$ and the slopes $\left(\frac{d(q/\theta)}{d\theta^{1/3}}\right)$ are $B'ka^{1/3}$. The convective modulus is therefore proportional to the cube of the ratio slope:intercept. But the convective modulus of any fluid is related to other physical properties by

$$a = \frac{gc\beta\rho^2}{\eta k} \dots\dots\dots (8)$$

and consequently may be computed from tables of these properties provided all are known. The quantity a usually varies rapidly with the temperature, increasing with a temperature rise in the case of a liquid and decreasing with a temperature rise in the case of a gas. For water at 27° C. a has the value

$$2.0 \times 10^4 \text{ cms.}^{-3} \text{ }^\circ\text{C.}^{-1}.$$

Experimental values for the various liquids tested compared with calculated values are given in Table IV as "relative convective moduli" or as a ratio of the convective moduli of the fluids concerned to that of water, both at 27° C.

Bearing in mind the fact that a 5% error in both the intercept and slope can lead to a 30% error in the measured convective moduli; there is, in most instances, excellent agreement between the measured and calculated convective moduli in Table IV. However, the agreement in the case of formic acid (of somewhat higher electrical conductivity than the other liquids studied) is not good; nor is it satisfactory in the case of the more volatile liquids, acetone, ethyl acetate, chloroform and carbon tetrachloride.

Summarizing the results of the last two sections, therefore, it appears that the method as suggested in this paper is capable of yielding accurate comparative figures for the thermal conductivities and convective moduli of liquids which are

TABLE IV.
Relative Convective Moduli at 27° C.

Fluid.	Relative Convective Moduli.	
	By Measurement.	By Computation from Physical Properties.
Water	1.00	1.00
96% Ethyl alcohol	6.3	6.3
Ethylene glycol	0.20	0.22
92% Glycerine	0.014	0.022
Methanol	10.6	9.3
Formic acid	0.14	1.4
Acetic acid 95%	7.8	5.6
Acetic anhydride	0.26	—
Acetone	6.5	18.0
Ethyl acetate	3.8	17.0
Benzene	9.5	10.0
Toluene	9.3	9.8
Carbon tetrachloride	7.3	15.0
Chloroform	3.0	16.0
Air.. .. .	0.003	0.005

not electrical conductors and are not too volatile. The method particularly commends itself to the comparison of the conductive and convective properties of binary mixtures and solutions of non-electrolytes.

COMPARISON WITH THE METHOD OF HUTCHINSON.

E. Hutchinson (1945) has proposed a hot-wire method for measuring the thermal conductivities of liquids based on one used by Bolland and Melville (1937) for the thermal conductivities of gases. Hutchinson uses a fine coiled coil filament axially in a narrow tube of the liquid under test. The wire is heated by a current of the order of 10 milliamps. and the measured temperature rise is only of the order of 1° C. Absolute values of the thermal conductivity may be calculated from the formula

$$q = \frac{\theta}{r} k \log r_1/r \dots\dots\dots (9)$$

where r is the radius of the wire and r₁ of the vessel.

Application of this equation assumes that convection currents are absent or that the Grashof numbers are small. There are three factors contributing to make this so. The temperature rise θ is low, the wires are fine, and they are used in the vertical position. Reference to Figures 1 and 2 above shows how very much less are the effects of convection from vertical as opposed to horizontal wires. As a matter of interest Hutchinson remarks that his results are erratic when the vessel is inclined at more than 25° to the vertical.

The method suggested in this paper differs from that of Hutchinson by the absence of near walls at a fixed temperature and by the measurement of a temperature difference between the surface of the wire and the bulk of the fluid. Comparison of equation (9) with the limiting form (equation 5) expressed in the form

$$q = 0.40 \frac{\theta k}{2r} \dots\dots\dots (5a)$$

may be used to give a measure to the thickness of the stagnant Langmuir film around the heated wire at low Grashof numbers. From a comparison of (9) and (5a) it follows that the effective external radius of the stagnant film is given by

$$\log_e r_{1,r} = 0.20$$

$$\text{or} \quad r_1 = 1.221r \dots\dots\dots (10)$$

SUMMARY.

A length of resistance wire is immersed in a fluid and heated by a current I . The heat input is proportional to I^2 and the temperature difference (θ) between bulk of fluid and the wire may be measured by means of a small thermocouple attached to the centre of the heated wire. When from data thus obtained I^2/θ is plotted against $\theta^{1/3}$ straight lines are obtained, the intercepts on the I^2/θ axis of which are proportional to the thermal conductivities of the fluids concerned while the ratios of the slopes to the intercepts are proportional to the cube root of the convective moduli.

The method is tested experimentally by measurements in fluids of known thermal conductivities and convective moduli. The results obtained show satisfactory agreement except from liquids of high electrical conductivity (resulting in short-circuiting of the thermocouple), or too high a volatility (which results in a cooling of the c.j. of the thermocouple).

The method has also been tested by drawing the I^2/θ versus θ curves for a number of different orientations of the wire in the one fluid. The curves obtained are similar in shape and have a common intercept and a slope which is a maximum when the wire is horizontal and a minimum when the wire is vertical.

The magnitude of the heat flow from a horizontal cylinder at vanishing temperature difference leads to a figure of $0.221 \times$ radius for the thickness of the stagnant film surrounding the cylinder.

It is suggested that the method outlined in this paper would be particularly valuable in a rapid assessment of the heat transfer properties of concentrated solutions of non-electrolytes.

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THE UNIFORM CONVERGENCE OF SEQUENCES OF MONOTONIC FUNCTIONS.

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(Communicated by PROFESSOR K. E. BULLEN.)

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The following result is due to G. Pólya*): If a sequence $f_n(x)$ of monotonic functions converges to a continuous function $f(x)$ in an interval $a \leq x \leq b$, then the convergence is uniform. It will be shown in the present paper that in the case of a discontinuous limit function $f(x)$ the uniform convergence can likewise be characterized in terms of ordinary convergence: the necessary and sufficient condition for uniform convergence is that both $f_n(x-0) \rightarrow f(x-0)$ and $f_n(x+0) \rightarrow f(x+0)$. More precisely:

If $f_n(x)$, $f(x)$ are defined and monotonic non-decreasing in $a \leq x \leq b$, then $f_n(x) \rightarrow f(x)$ uniformly in $a \leq x \leq b$ if and only if

(1) $f_n(x) \rightarrow f(x)$ for all x of an everywhere dense set E in $a \leq x \leq b$ containing the set D of all discontinuity points of $f(x)$

and

(2) $f_n(x-0) \rightarrow f(x-0)$, $f_n(x+0) \rightarrow f(x+0)$ for all x in D .

Proof.

1. Let $f_n(x) \rightarrow f(x)$ uniformly. (2) only has to be proved. Actually (2) holds uniformly in $a \leq x \leq b$: to any $\varepsilon > 0$, $N(\varepsilon)$ exists such that

$$|f(t) - f_n(t)| < \varepsilon \text{ for } n > N \text{ and } a \leq t \leq b,$$

whence

$$\lim_{t \rightarrow x \pm 0} |f(t) - f_n(t)| = |f(x \pm 0) - f_n(x \pm 0)| \leq \varepsilon.$$

2. Let (1), (2) hold. It will first be shown that (1), (2) hold for all x in the interval. As (1), (2) hold on D it is sufficient to consider the continuity points of $f(x)$. Let x be a continuity point.

To any $\varepsilon > 0$, t_1, t_2 exist in E such that $t_1 < x < t_2$ and

$$f(x) - \frac{\varepsilon}{2} \leq f(t_1) \leq f(t_2) \leq f(x) + \frac{\varepsilon}{2}.$$

By (1), N exists such that

$$|f(t_i) - f_n(t_i)| < \frac{\varepsilon}{2} \text{ for } n > N, i=1, 2.$$

Hence

$$f(x) - \varepsilon \leq f_n(t_1) \leq f_n(x-0) \leq f_n(x) \leq f_n(x+0) \leq f_n(t_2) \leq f(x) + \varepsilon,$$

whence

$$\lim_{n \rightarrow \infty} f_n(x-0) = \lim_{n \rightarrow \infty} f_n(x) = \lim_{n \rightarrow \infty} f_n(x+0) = f(x) = f(x-0) = f(x+0).$$

* Ueber den zentralen Grenzwertsatz der Wahrscheinlichkeitsrechnung und das Momentenproblem, *Mathematische Zeitschrift* 8 (1920), pp. 171-181.

It will now be shown that the assumption of non-uniform convergence leads to a contradiction. In the case of non-uniform convergence, $\epsilon > 0$, a sequence of integers $n_1 < n_2 < n_3 < \dots$ and a sequence of real numbers x_1, x_2, x_3, \dots in $a \leq x \leq b$ exist such that

$$(3) \quad |f(x_k) - f_{n_k}(x_k)| \geq \epsilon \text{ for } k=1, 2, 3, \dots$$

The x_k have at least one limit point t in the interval, and it may be assumed that $x_k \rightarrow t$. At most a finite number of the x_k can be equal to t ; for, by (1), $f_n(t) \rightarrow f(t)$, i.e. $|f(t) - f_n(t)| < \epsilon$ for $n > N$, and (3) shows that $x_k \neq t$ for $n_k > N$. Hence, an infinite subsequence of the x_k exists whose terms are either all less or all greater than t . It is sufficient to consider the first case. Choosing $\delta > 0$ such that

$$0 \leq f(t-0) - f(t-\delta) < \frac{\epsilon}{2},$$

K exists such that

$$t - \delta \leq x_K < t, \quad |f(t-\delta) - f_{n_K}(t-\delta)| < \frac{\epsilon}{2}, \quad \text{and} \quad |f(t-0) - f_{n_K}(t-0)| < \frac{\epsilon}{2},$$

whence

$$\begin{aligned} f(x_K) - f_{n_K}(x_K) &\leq f(t-0) - f_{n_K}(t-\delta) \\ &= f(t-0) - f(t-\delta) + f(t-\delta) - f_{n_K}(t-\delta) < \epsilon, \end{aligned}$$

and

$$\begin{aligned} f(x_K) - f_{n_K}(x_K) &\geq f(t-\delta) - f_{n_K}(t-0) \\ &= f(t-\delta) - f(t-0) + f(t-0) - f_{n_K}(t-0) > -\epsilon \end{aligned}$$

which contradicts (3).

Pólya's result is a corollary, as for continuous $f(x)$ condition (2) is vacuous.

The result may be extended to sequences $f_n(x)$ which are defined for $-\infty < x < \infty$ and converge to a bounded function $f(x)$. Using a transformation like $x = \tan y$, and applying the above result to the interval $-\frac{\pi}{2} \leq y \leq \frac{\pi}{2}$, it is seen that the only additional condition required is

$$\lim_{n \rightarrow \infty} (\lim_{x \rightarrow \pm \infty} f_n(x)) = \lim_{x \rightarrow \pm \infty} f(x).$$

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July, 1947.

A METHOD OF DETERMINING THE DISTRIBUTION OF OIL IN A RESERVOIR ROCK BY MEANS OF ULTRA-VIOLET LIGHT.

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INTRODUCTION.

The fluorescent properties of both crude and refined oils under ultra-violet light are well-known and have been used in petroleum technology in America and Germany. The value of ultra-violet light in the preliminary examination of drill cores to detect the presence of oil has also been appreciated but there is apparently no record in oil literature of the use of ultra-violet light to determine the detailed distribution of oil in a reservoir rock.

In 1945 the author collaborated with Mr. R. F. Thyer, Geophysicist, in an investigation of the reservoir properties of portion of the oil-bearing glauconitic sandstone at Lakes Entrance, Victoria. The investigation included a detailed examination of drill cores from the reservoir rock and, subsequently, an inspection of the reservoir rock *in situ* in exposures at the bottom of the Lakes Entrance oil shaft. Ultra-violet light was used to determine the detailed distribution of oil in the rock, both in cores and *in situ*. As yet the author is not at liberty to disclose the results of the investigation, but the techniques adopted are described in this paper as they may be of interest to other workers.

It should be remembered, however, that this method of core analysis was developed to deal with a reservoir rock in which oil was, for the most part, invisible, and in very small quantities. The method has, therefore, a limited application in oil technology although it could be adopted to deal with reservoir rocks with different characteristics. Notes on the examination of the rock *in situ* are included for their interest rather than utility, since very few oil fields could present a geologist with such unique opportunities.

EXAMINATION OF DRILL CORES BY ULTRA-VIOLET LIGHT.

General.

During the investigation at Lakes Entrance a diamond drill hole, termed the "Shaft Bore", was drilled from the bottom of a shaft to penetrate a thickness of 19 ft. 2½ in. of the oil-bearing glauconitic sandstone. The glauconitic sandstone was cored in sections approximately 2 ft. long and 1½ in. in diameter. Each core was transferred directly from the core barrel to a special air-tight container and then taken to Canberra, where the cores were analysed.

Previous experience in drilling at Lakes Entrance indicated that some cores from the glauconitic sandstone, when first removed from the core barrel, carried brown oily patches on the surface which disappeared after exposure to the air. Furthermore, no oil could be detected by eye or by microscope when these cores were subsequently examined in the laboratory—presumably because the small quantity of oil present was in a finely divided state and could not be detected against the background of green glauconitic sandstone.

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Most of the cores of glauconitic sandstone from the Shaft Bore showed patches of oil on the surface when first removed from the core barrel and the position and extent of each patch were carefully logged because the oil appeared to indicate the position of oil-bearing sandstone. However, these patches were no longer visible when the cores were unsealed in the laboratory some weeks later and it was at this stage that ultra-violet light was first used. Its value was at once apparent, firstly as a means of relocating the oily patches on the surface of the cores and subsequently as a means of establishing the detailed distribution of oil in the sandstone.

Ultra-violet Light Equipment.

In the experimental stages the cores were examined under two types of ultra-violet lamp: the "Mineralight" lamp and the "Mercera" lamp. The "Mineralight" equipment consists essentially of a coiled quartz tube in which a cold electric discharge through mercury vapour takes place. Electric power may be obtained either from batteries or from the 240 volt A.C. main supply with suitable transformer. The lamp is rated at 30 watts and is fitted with a filter constructed from a type of glass known as "Red Purple Corex A No. 986". The ultra-violet light emitted mostly corresponds to a wave-length of 2537 Å.

The "Mercera" lamp provides a source of near ultra-violet light and no appreciable amount is emitted below a wave-length of about 3100 Å. The equipment consists of a mercury vapour lamp enclosed in a dark glass envelope, which absorbs most of the visible light. The lamp which was used is rated at 80 watts and, in association with a choke coil, operates from the 240 volt A.C. main supply.

Crude and refined oils fluoresce under both lights, but the fluorescence is distinctly brighter under the "Mercera" lamp, which was therefore used throughout the investigation. Under this lamp portions of the core which contain oil show a yellow to a pale yellowy-brown fluorescence, apparently dependent upon the proportion of the rock surface actually covered with oil and on the thickness of the oil films.

Several tests were carried out to ensure that this fluorescence was actually produced by crude oil in the core and not by any of the other substances known to be present. Glucose solution had been introduced into the drilling water as an index chemical and mercuric chloride and merthiolate solution had been used to inhibit fermentation of any glucose penetrating the cores. Each of these substances was tested under ultra-violet light and showed no fluorescence. Next a few fragments of fluorescent and apparently oil-bearing core were placed in a test tube stoppered with cotton wool. Neither tube nor stopper showed any fluorescence under ultra-violet light. The test tube was then heated for a few minutes, cooled, and both tube and stopper bore a condensate which gave a bluish-white fluorescence typical of oil distillates. The fragments of core were also examined after heating and found to have lost all fluorescence under ultra-violet light. A further experiment was carried out using "Shellite" solvent to remove oil from a portion of fluorescent core, and after drying at low temperature, the core no longer showed fluorescence. Finally a portion of the core showing no fluorescence was impregnated with Lakes Entrance oil and the resulting fluorescence was identical with that found elsewhere in the cores.

It should be noted that special spectacles with side shields were worn while using the lamp to protect the eyes from damage by concentrated ultra-violet light.

Procedure.

In the first series of tests carried out at Canberra the external surface of the cores were examined under ultra-violet light. The unbroken core was placed

horizontally in an adjustable core holder which allowed rotation of the core about its principal axis. The examination was carried out in the dark room and the cores were returned to their sealed containers as soon as possible.

Oily patches originally observed on the surface of the cores could be relocated under ultra-violet light and the distribution of fluorescent patches on the complete surface of the core was portrayed on three columnar sections, each being a projection on to a horizontal plane of one-third of the surface of the core.

The resulting core diagrams provided a clear picture of the distribution of oil on the surface of the cores. However, later work showed that these diagrams, although they indicated roughly the location of the principal oil-bearing zones, did not present a true picture of the original distribution of oil in the rock, because, in many cores, oil which had welled out of portion of a core during drilling and recovery had either gravitated down the surface of the core or had been spread by the core catcher over a larger area than it had originally occupied. The distribution of oil on the surface could also have been effected during handling or by movement within the containers.

This method was therefore replaced by one which dealt solely with unexposed sections of the core.

In the procedure finally adopted the cores were removed from the containers, cut into sections approximately 3 in. in length, and stored in small bottles with air-tight caps. This made handling easier and reduced the total period of time that cores were exposed to the air during examination. To enable these sections to be oriented a heavy pencil line was drawn longitudinally along the surface of the core before it was cut.

Each section examined was then cut into thin discs approximately $\frac{1}{4}$ in. in thickness by means of a special core cutter. This consisted of a pair of semi-circular steel chisels with a radius of curvature approximately the same as that of the core. The core was held in a vice and the chisels fitted over it to provide a disc of the correct thickness. The core could then be broken cleanly by one sharp blow with a hammer.

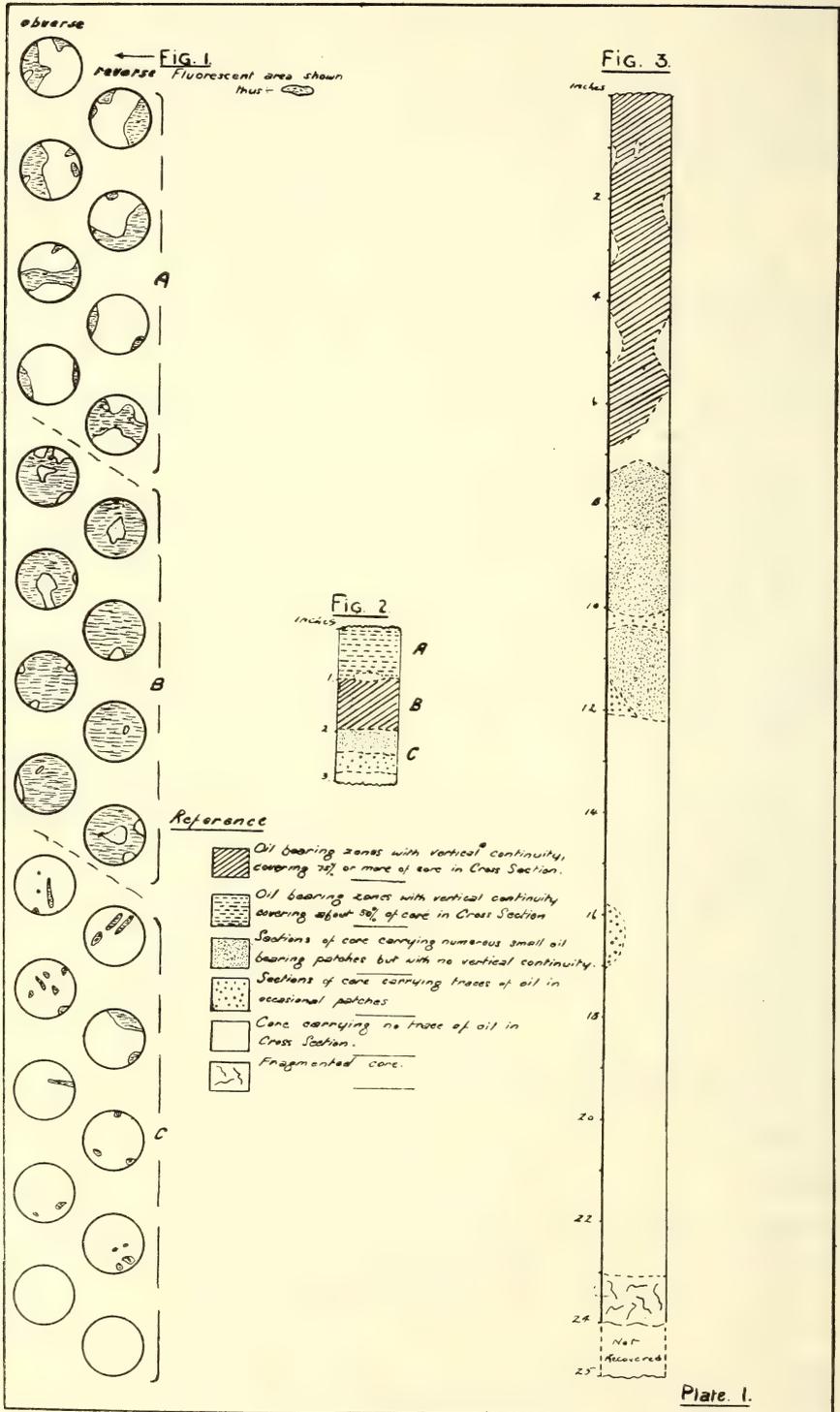
By means of the pencil line mentioned above, each disc cut from the core section could be placed in correct orientation. The suite of discs so obtained (10 to 12 discs for each 3 in. core section) was examined under ultra-violet light and fluorescent areas showing on each were plotted on a sheet bearing a series of circles representing cross-sections of the core at half natural size. Both obverse and reverse sides were examined to provide two series of diagrams from which the distribution of oil within the core could be established. Fluorescent patches on the discs were shown as stippled areas approximately to scale on the circular diagram but variations in the intensity of fluorescence were not depicted. A set of diagrams representing 3 in. of core are shown in Figure 1.

The fluorescent pattern was then examined to determine—

- (a) The general distribution of oil in cross-section.
- (b) The approximate percentage of cross-sectional area showing oil.
- (c) Whether oil-bearing patches had vertical continuity through two or more discs.

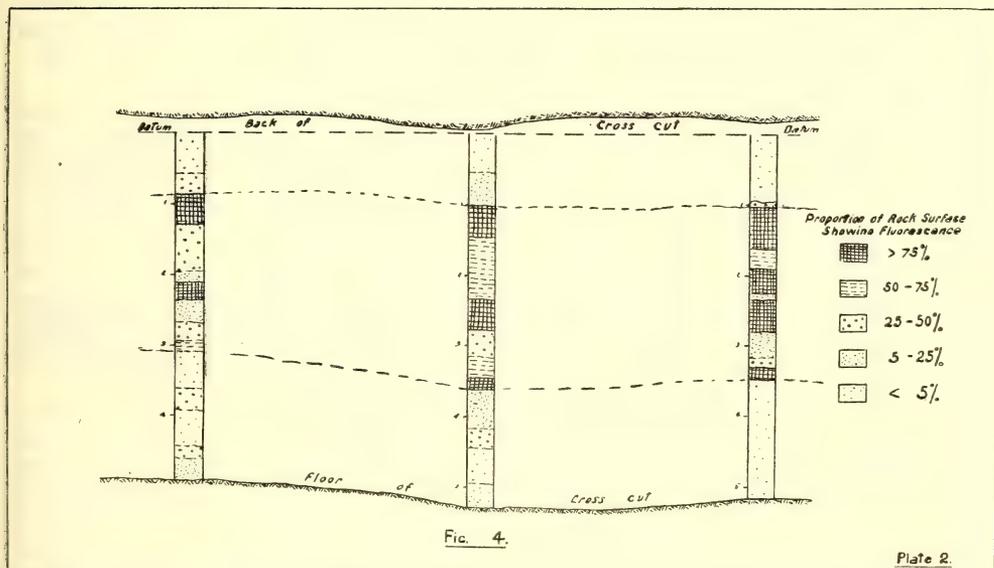
The core section could then be classified into one or more of the following five grades :

- (1) Oil-bearing patches covering 75 per cent. or more of the core in cross-section and with vertical continuity.
- (2) Oil-bearing patches covering approximately 50 to 75 per cent. of the core in cross-section and with vertical continuity.
- (3) Sections of core carrying numerous small oil-bearing patches with no vertical continuity.
- (4) Sections of core carrying a few oil-bearing patches.
- (5) Core carrying no oil in cross-section.



Finally this information was transferred to a columnar section on half natural vertical scale (Figure 2). This section was taken to represent a vertical plane passing through the centre of the core and the distribution of oil in the core, as established from the discs, was projected somewhat diagrammatically thereon. By this method a columnar section was constructed for each of the cores examined and one of these completed core diagrams is shown in Figure 3. More elaborate methods of portrayal, such as three-dimensional diagrams, could readily be devised, but where a large number of cores is involved a simple means of portrayal is important.

A generalized columnar section of the whole 19 ft. 2 in. of sandstone penetrated was then prepared from these individual columnar sections using a



simplified classification which divided the sandstone into major oil-bearing zones, minor oil-bearing zones, sandstone carrying isolated patches of oil and sandstone carrying no trace of oil.

Ultra-violet light examinations were followed by tests to determine the percentage oil saturation and these closely confirmed the quantitative work described above. The delineation of oil-bearing patches of sandstone by ultra-violet light also aided in petrological work and the essential difference between oil-bearing and barren rock could be determined. Ultra-violet and ordinary electric lights were arranged over a microscope in a dark room. Discs cut from the cores were placed on the microscope stage, and barren and oil-bearing portions compared after they had been defined by ultra-violet light.

USE OF ULTRA-VIOLET LIGHT UNDERGROUND.

The oil-bearing sandstone at Lakes Entrance does not outcrop, but in November, 1945, a winze sunk from the bottom of the oil shaft penetrated approximately 15 ft. into this formation and provided the first opportunity of examining the rock *in situ*.

Ultra-violet light was again used in a series of detailed examinations to delineate the oil-bearing portions of the rock. It was not possible to use the

"Mercera" lamp for this work since it was not adapted to operate from batteries, so a "Mineralight" was employed and powered from a 6-volt car battery.

Since oil was oozing from numerous patches in the section of rock exposed, the whole surface of the rock became covered with oil and care had to be taken to prepare a clean section for examination. A vertical channel about 6 in. wide and 1 in. to 2 in. deep was picked in the sandstone. A measuring tape was suspended from a nail inserted at a datum point at the top of the channel and the section then examined under ultra-violet light. The light was operated by an assistant while the observer logged the channel into sections and estimated the percentage area of fluorescence in each section. Short cross-cuts were eventually driven in the uppermost beds of the sandstone and vertical sections were cut and examined every 4 ft. along the walls and faces of the cross-cuts. Each vertical section was plotted to scale in the office and from the individual observations longitudinal sections and cross-sections of the workings were constructed to provide a clear picture of the distribution of oil in the rock. Three of these vertical sections are reproduced in Figure 4.

The distribution of oil established by this work agreed within very close limits with that already determined from the diamond drill cores in the same section of rock. Thus the underground work constituted a valuable check on the veracity of the earlier determinations which were based on the cores from a single drill hole.

ACKNOWLEDGMENTS.

The writer is indebted to Mr. R. F. Thyer for many helpful suggestions during the original investigation and for his criticism of this paper. Thanks are also accorded to the Director of the Bureau of Mineral Resources, Dr. H. G. Raggatt, for his permission to publish the work.

SPECTROSCOPIC CHARACTERISTICS OF ORDINARY ACHESON GRAPHITE.

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INTRODUCTION.

This report considers the suitability of ordinary low-grade Acheson graphite for spectrographic electrodes. The characteristics investigated were purity and homogeneity. Attempts to purify the graphite by chemical treatment are also reported.

The main point of this paper is a quantitative statement of results in terms of relative intensities of impurity lines before and after treatment. In the past there has been a considerable divergence of opinion among spectrochemists as to what constitutes an "adequate" purification process.⁽¹⁻¹⁰⁾ The use of various kinds and qualities of graphite and carbon differing widely in natural purity, together with the lack of quantitative data, has made a proper comparison of methods of purification impossible.

In attempting to avoid these difficulties, results have been (1) stated quantitatively, both as regards average intensities of impurity lines and also probable deviations from the average, (2) compared with Hilger H.S. brand graphite, which is accepted as suitable for most spectrographic analysis. (It should be emphasized that in making comparison with Hilger graphite absolutely no reflection is intended on the manufacturers of Acheson graphite. The Acheson brand tested is a low-grade one certainly never intended for spectroscopic use. It is very cheap in comparison with Hilger H.S. brand, which is supplied specifically for spectroscopy.)

All spectrograms were taken with a Hilger E179 one-metre quartz spectrograph and densities measured with a Zeiss microphotometer.

PURITY.

Specially purified graphite rods can be purchased from several manufacturers. These are usually expensive and were also in very short supply in Australia during the war, facts which obliged the writer to consider using ordinary Acheson graphite whenever possible.

$\frac{1}{4}$ in. and $\frac{3}{8}$ in. diameter Acheson rods were examined. These were broken to $\frac{5}{8}$ in. lengths and the broken faces arced at 10 amps.

As most of the analytical work of this laboratory has been confined to the spectral region 5000—2000 Å.U., the rods were examined only in this range. Elements detected were Ca, Cu, Ti, V, Al, Si, Mg, Fe, B. All of these could also be detected in the Hilger graphite. Both sizes of each type are included as there is some indication that the larger size is purer.

One line representative of each impurity element has been measured in density relative to background for each spectrum considered. For the purpose of comparison the intensity of each line has been taken as unity for the $\frac{1}{4}$ in. Acheson rods, relative intensities for the other three rods being found by conventional methods of photographic photometry. Figures quoted in Table 1

are average intensities based on 10 arcings for each type of rod. Intensities are measured always for light from the arc column. Some figures for Hilger rods are very doubtful, these lines being barely distinguishable against the background and on the limit of sensitivity of the microphotometer.

TABLE 1.

Element.	Wave-length. V.U. (M.I.T.).	A. Acheson $\frac{1}{4}$ in.	B. Acheson $\frac{3}{8}$ in.	C. Hilger $\frac{1}{4}$ in.	D. Hilger $\frac{3}{8}$ in.	E. Acheson $\frac{1}{4}$ in. 3-day HCl.	F. Acheson $\frac{1}{4}$ in. 1-day HNO ₃ .	G. Acheson $\frac{1}{4}$ in. 4-day HNO ₃ .
Ca	4226·728	1·00	0·81	1·12	0·54	0·2	0·6	0·3
Cu	3247·540	1·00	0·81	0·72	0·58	0·7	0·7	0·6
Ti	3234·52	1·00	0·82	0·49	0·36	0·6	0·5	0·4
V	3102·299	1·00	1·2	0·74	0·72	0·7	0·8	0·6
Al	3082·155	1·00	0·68	0·49	0·47	0·6	0·7	0·5
Si	2881·578	1·00	1·1	0·51	0·22	1·0	0·9 (?)	1·0
Mg	2852·129	1·00	1·78	4·47	0·36	0·5	0·5	0·3
Fe	2599·39	1·00	0·69	0·29	0·28	0·3	0·6	0·3
B	2497·733	1·00	1·2	1·2	1·0	1·5 (?)	1·3 (?)	1·4 (?)

The relative impurity of the Acheson rods is evident from these figures. In particular, the difference in the degree of development of the iron spectrum corresponding to intensities 1·0 and 0·28 is considerable at this level of intensity, affecting very seriously the use of this Acheson graphite for analytical purposes.

HOMOGENEITY.

Repeated arcings showed that Acheson rods were very inhomogeneous. The better rods compared favourably with Hilger rods, while the worst gave well-developed spectra of all the above elements.

On the other hand, Hilger rods prepared for arcing in exactly the same way always gave similar spectra as regards most elements, so that the impurity was not due to chance contamination in the laboratory of occasional rods.

This is expressed in Table 2, which compares Acheson and Hilger $\frac{1}{4}$ in. rods. Individual intensities (I_1, I_2, \dots, I_{10}) of the same 10 arcings were calculated and the probable deviation ΔI from the mean \bar{I} of a single arcing calculated by

$$\Delta I = \pm 0.67 \sqrt{\frac{\sum_{i=1}^{10} (\bar{I} - I_i)^2}{9}}$$
 To emphasize the difference mean intensities were corrected to unity for both types.

TABLE 2.

Element.	Acheson $\frac{1}{4}$ in.	Hilger $\frac{1}{4}$ in.
Ca	1·00 ± 0·15	1·00 ± 0·12
Cu	0·15	0·22
Ti	0·51	0·10
V	0·24	0·11
Al	0·22	0·02
Si	0·21	0·16
Mg	0·18	0·15
Fe	0·57	0·05
B	0·14	0·09

Some elements are obviously quite unpredictable in Acheson rods, especially Fe. Hilger rods are less reliable only as regards copper. Occasional rods show copper lines moderately intense. Danger of contamination was very slight, in fact the Hilger rods were kept in their original packing until the time of use. In all these experiments they were broken to correct lengths (not machined in any way) and the broken surfaces arced.

The inhomogeneity is really more serious than the impurity itself. Rods of known state of purity can often be used in spectroscopic work by photographing the blank spectrum alongside. With Acheson rods a blank spectrum would be useless, as it would represent only the tip of the rod actually burned during the exposure. A pocket of impurity lying below the surface would be exposed by continued arcing. This sort of thing has in fact been observed repeatedly. So-called "jumping plate" spectra were taken, i.e. the plate-holder was racked at regular intervals of time while the arc burned.

Figure 1 shows some curious results obtained in this way. These are plots of line density relative to background, against burning time. All plots are from the same plate and hence show simultaneous behaviour of the elements. A quite striking feature is the correspondence between certain elements, viz. Ti, V, Al, Si. (Ca, Fe, Mg may also be correlated with this group—other plates did not always confirm these, however.)

Presumably these impurities occur together in pockets due in some way to the method of manufacture of the graphite. Copper and boron seem generally to be unrelated to this scheme. All plates of Acheson graphite have shown this behaviour to a greater or lesser extent and the effect is believed to be real. Fluctuations observed in Hilger arcings were not large enough to observe any obvious correlation between impurity elements. Figure 1 shows Ca, Si, B only. There is a general trend due to fractional distillation in the arc removing the more volatile elements and concentrating B.

CHEMICAL PURIFICATION.

For operation on a small scale a pyrex extractor was ideal. This periodically refluxed the rods with distilled acid. Rods broken or cut to final form were placed in the extractor space. The various solvents placed in the lower reservoir were boiled by a gas ring or electric hot-plate regulated to cause the 500 c.c. soxhlet to reflux about every 30 minutes. Approximately 10 pairs of rods were treated at a time. One shortcoming of the soxhlet is that it tends to give unequal treatment due to the rods at the bottom of the pile being immersed longer while the liquid builds up to the siphoning level. During a prolonged treatment the condenser was removed at least twice per day and the electrodes stirred well with a silica rod.

After solvent treatment electrodes were boiled for several hours in successive washes of distilled water.

The scope of chemical treatment tried here has not been extensive and figures are given only for HCl and HNO₃. These solvents require only the simplest equipment and a minimum of attention and are much more agreeable to work with than H₂SO₄. The latter, with its high boiling point, requires the soxhlet to be lagged and also all sorts of precautions need to be taken as the rods tend to disintegrate during treatment.

To ensure that the chemical processes themselves were not introducing impurities the obvious precaution was taken of subjecting Hilger rods to the same treatment. These always emerged slightly improved as regards most elements, but never worse.

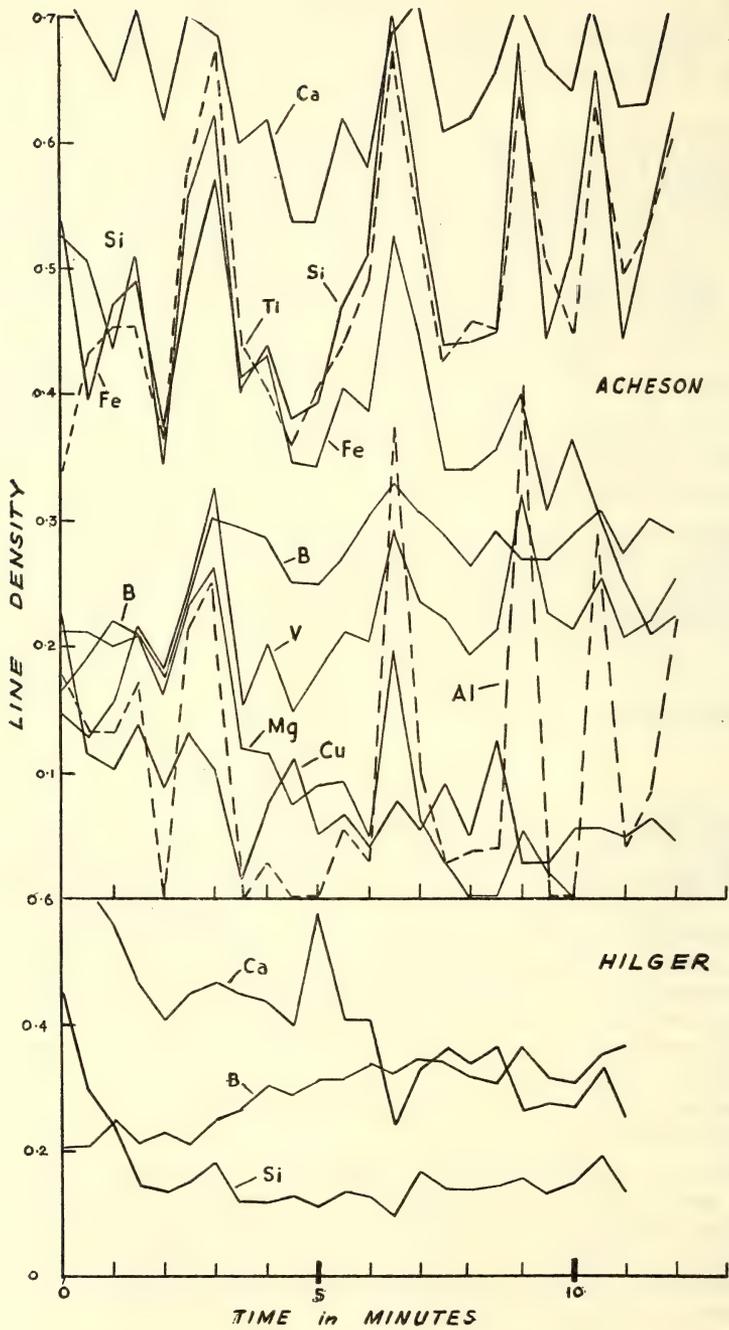


Fig. 1.

RESULTS:

Continuing the method of recording used in columns A and D of Table 1, i.e. taking the intensity with untreated Acheson graphite $\frac{1}{4}$ in. as unity intensity, the last three columns (E, F, G) give the intensities of impurity lines after chemical treatment with HCl (3 days) and HNO₃ (1 and 4 days). Averages from about 10 arcings are given in each case.

It is seen that an *average* purity similar to that of Hilger rods can be obtained for most elements (except B and Si) by either HCl or HNO₃ soxhlet treatment for 3-4 days. Such rods are still inhomogeneous and too unreliable for most work.

Uniformly reliable rods *never* exceeding the impurity of Hilger graphite require 12-15 days of either HCl or HNO₃ (neither acid seems to show any marked superiority for this purpose). This duration of the treatment results in average intensities of the order of 0.1, certainly superior to Hilger rods. These rods are highly satisfactory. The treatment is very lengthy but requires practically no supervision once in operation. Residual lines showing in occasional spectra are chiefly Fe, 2599.39, 2598.37; Ti, 3234.52, 3236.58, 3239.04, 3241.98; Mg, 2852.129 together with B, Si. Ca lines which are very persistent can usually be wholly removed by this treatment.

Aqua-regia does not significantly improve the figures quoted for HCl and HNO₃. None of the above chemical treatments adversely affects the final rods in any way.

H₂SO₄ is unsuited to the soxhlet method and boiling the electrodes in a flask requires a large number of washes to be effective and is very extravagant with acid. A few trials made here showed it to be more effective in removing Ti and V (Ti especially is a troublesome and irregular residual). No quantitative data have been accumulated for H₂SO₄ treatment. B and Si are present in both the Hilger and the Acheson graphite and are probably untouched by any acid treatment. Table 1 actually shows a rise in the B line intensity. This is almost certainly spurious, due to B carrying more of the electric arc when the more volatile elements are removed.

Methyl alcohol treatment for as long as two months did not reduce B.

PRE-ARCING.

This has been recommended by many spectroscopists and is very advisable as most of the graphs of Fig. 1 show. There is an initial drop in line density during the first few minutes of arcing.

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THE PETROLOGY OF THE SILURIAN VOLCANIC SEQUENCE AT WELLINGTON, N.S.W.

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With five Text-figures and two Tables.

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1. INTRODUCTION.

The volcanic sequence which is to be discussed in this paper lies to the north-east, east and south-east of the town of Wellington and crops out in the parishes of Micketymulga, Wellington, Bodangora and Wuuluman. The rocks are of Silurian age and form part of a volcanic belt which extends from the Jurassic sandstone near Geurie southwards through Wellington and Molong. The volcanic rocks of Orange, Cargo, Parkes, Forbes and Cobar are probably the same age.

Very little petrological work has been done on the Silurian lavas and tuffs of New South Wales and it has been tacitly assumed that they have been much altered since their formation; this study reveals that many of the low-grade minerals present in the lavas are due to deuteritic activity. It is hoped that the proof of this fact, as well as the petrological data collected, will be of value in furthering the knowledge of these rocks.

I wish to thank Dr. G. A. Joplin and Dr. W. R. Browne, of Sydney University, for the help and encouragement they have given during the preparation of this paper, and Elizabeth M. Basnett for the preparation of Figs. 2 and 3.

2. FIELD OCCURRENCE.

The outcrops between Wellington and Wuuluman consist of Silurian lavas interbedded with pyroclastic rocks and an overlying series of limestones, tuffs, breccias, slates and felsitic rhyolites. These have been named the Volcanic

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Series and Upper Sedimentary Series respectively (Basnett and Colditz, 1945). The whole sequence is folded into plunging anticlines and synclines from which alternating sub-meridional outcrops have been produced by erosion.

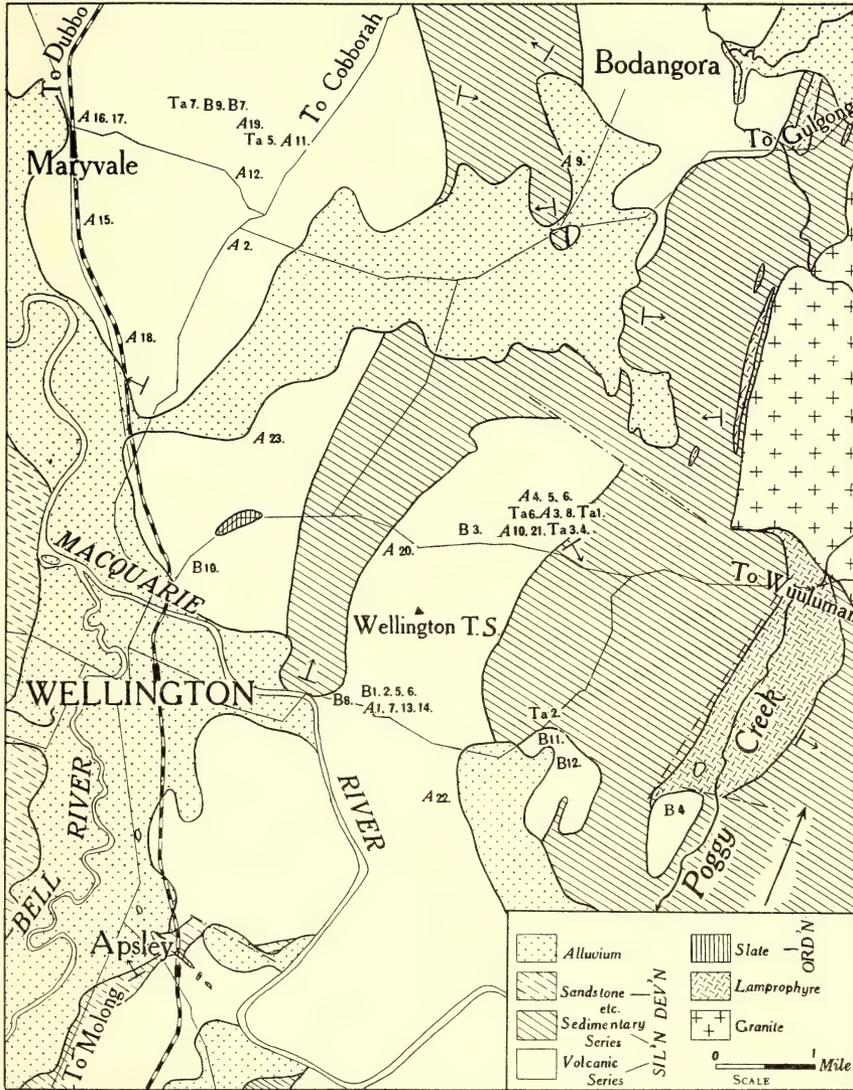


Fig. 1.—A Simplified Geological Map showing the Volcanic Series.

The Sedimentary series has been intruded by a number of sills of augite-lamprophyre (Basnett, 1942) which are believed to have a close genetic relationship to the lava flows and are included with them in the chemical discussion. The sills occur as lens-like outcrops of varying dimensions and are to be found to the east and north-east of Wellington.

The Volcanic Series can be traced beyond the confines of the map both to the north and south. Northwards the lavas are covered by the Jurassic strata at Geurie and southwards they continue towards Molong, which is 35 miles

distant. West of the Catombal Range narrow flows are found and these seem to be on the same horizon though they are more limited in thickness.

Within the series there seems to be no lava flow sufficiently continuous or distinctive to serve as a datum horizon for mapping since individual flows often merge into breccias or into xenolith-bearing flows or they may be covered with soil and alluvium. This being the case, it has so far been found impossible to examine the lava-succession over any appreciable area and collecting has been necessarily rather haphazard. However, it has been possible to examine a fairly complete sequence to the east of Maryvale in Pors. 138, 133, 182 and 123, Par. Micketymulga. It is as follows:

Glassy augite andesite (A16).

Augite andesite with albitised feldspars and vughs. Flow structure is shown by the orientation of the feldspars (A17).

Boulders from the weathering of a volcanic agglomerate.

Hornblende pyroxene trachyandesite (T7).

Porphyritic basalt (B9).

A finer phase of B9 containing rounded inclusions of the porphyritic basalt.

Porphyritic basalt (B7).

Augite andesite (A19).

Hornblende trachyandesite (T5).

Augite hornblende andesite (A11).

Volcanic agglomerate.

(The numbers used here and throughout the paper refer to Table I, which lists the type collection of slides in the museum of the Geology Department, Sydney University.)

3. LAVAS.

(i) Nomenclature.

As only three chemical analyses of the lavas have been made it has been found necessary to name and group them by petrographic methods. About 100 microscope sections have been examined, specific gravity determinations have been made and staining tests for orthoclase have been carried out (Gabriel and Cox, 1929).

The three analysed rocks are hornblende trachyandesite, augite hornblende andesite and porphyritic basalt (Table II) with silica percentages of 63, 57 and 50 and specific gravities of 2.74, 2.77 and 2.92 respectively. Petrological examination and a comparison of the specific gravities suggest that most other lavas examined are comparable with these three types, and it is assumed that they would also compare in chemical composition.

The trachyandesites and andesites are subdivided on the basis of their ferromagnesian minerals, e.g. hornblende, hornblende augite and augite andesites are found. Those rocks which contain orthoclase either in the groundmass or as phenocrysts have been named trachyandesites or trachybasalts, whilst the basalts are distinguished from the andesites by the development of an appreciable amount of augite in the groundmass, by the presence of abundant large phenocrysts of augite and by their higher specific gravities.

(ii) Petrography.

Trachyandesites.

The most acid of the trachyandesites has a sp. gr. of 2.71 and contains phenocrysts of albitic plagioclase with some orthoclase. Hornblende and augite are absent but chlorite and iron ore are developed together with much deuteric quartz and carbonates. The groundmass has a mineralogical composition similar to that of the phenocrysts.

TABLE I.

Table of Specific Gravities and Localities.

Number.	Sp. Gr.	Locality.	Name.
T1	2.71	Por. 76, Par. Nanima.	Trachyandesite.
T2	—	Por. 86, Par. Nanima.	Trachyandesite.
T3	2.74	Por. 94/122, Par. Nanima.	Hornblende trachyandesite. (Analysed.)
T4	2.75	Por. 94, Par. Nanima.	Hornblende trachyandesite.
T5	2.77	Por. 123, Par. Micketymulga.	Hornblende trachyandesite.
T6	2.75	Por. 94, Par. Nanima.	Hornblende trachyandesite.
T7	2.87	Por. 182, Par. Micketymulga.	Hornblende augite trachyandesite.
A1	2.76	Por. 31, Par. Nanima.	Hornblende andesite.
A2	—	Por. 1, Par. Nanima.	Hornblende andesite.
A3	—	Por. 94, Par. Nanima.	Hornblende andesite.
A4	—	Por. 94, Par. Nanima.	Hornblende andesite.
A5	—	Por. 94, Par. Nanima.	Hornblende andesite.
A6	—	Por. 94, Par. Nanima.	Hornblende andesite.
A7	—	Por. 31, Par. Nanima.	Hornblende andesite.
A8	2.76	Por. 94, Par. Nanima.	Hornblende andesite.
A9	—	Bodangora Common.	Hornblende andesite.
A10	—	Por. 94/122, Par. Nanima.	Hornblende andesite (in breccia).
A10a	—	Por. 31, Par. Nanima.	Altered hornblende andesite.
A11	2.75	Por. 123, Par. Micketymulga.	Augite hornblende andesite.
A12	2.77	Por. 251, Par. Micketymulga.	Augite hornblende andesite. (Analysed.)
A13	2.80	Por. 31, Par. Nanima.	Augite hornblende andesite.
A14	2.88	Por. 31, Par. Nanima.	Augite hornblende andesite.
A15	—	Por. 73, Par. Micketymulga.	Augite hornblende andesite.
A16	2.81	Por. 133, Par. Micketymulga.	Glassy augite andesite.
A17	2.84	Por. 138, Par. Micketymulga.	Augite andesite.
A18	2.87	Por. 74, Par. Micketymulga.	Augite andesite.
A19	2.92	Por. 123, Par. Micketymulga.	Augite andesite.
A20	—	Por. 23, Par. Nanima.	Augite andesite.
A21	—	Por. 94, Par. Nanima.	Augite andesite.
A22	—	Por. 51, Par. Nanima.	Glassy augite andesite.
A23	2.91	Por. 1, Par. Nanima.	Glassy augite andesite.
B1	—	Por. 31, Par. Nanima.	Basalt.
B2	2.82	Por. 31, Par. Nanima.	Porphyritic basalt.
B3	2.92	Por. 93, Par. Nanima.	Porphyritic basalt. (Analysed.)
B4	2.97	Por. 50, Par. Nanima.	Porphyritic basalt.
B5	2.97	Por. 31, Par. Nanima.	Porphyritic basalt.
B6	—	Por. 31, Par. Nanima.	Porphyritic basalt.
B7	2.99	Por. 182, Par. Micketymulga.	Porphyritic basalt.
B8	3.00	Por. 31, Par. Nanima.	Porphyritic basalt.
B9	3.02	Por. 182, Par. Micketymulga.	Porphyritic basalt.
B10	—	Near Golf Links.	Porphyritic basalt.
B11	2.83	Por. 49, Par. Nanima.	Porphyritic trachybasalt.
B12	2.92	Por. 49, Par. Nanima.	Porphyritic trachybasalt.

The hornblende trachyandesites are the most commonly developed of this group of lavas and one of these has been analysed (Table 2). The most basic type sectioned contains orthoclase in the groundmass and not as phenocrysts and has a sp. gr. of 2.87. This high density is probably due to the fact that hornblende is almost completely resorbed to iron ore.

In hand specimen the trachyandesites are grey, aphanitic rocks with macroscopic phenocrysts of glassy or cream-coloured felspar and black ferromagnesian minerals. These phenocrysts may show parallelism in their arrange-

ment and deuteric alteration is indicated by the presence of light patches and irregular veins in the rock.

Thin sections reveal that the groundmass consists of tiny feldspar laths which show trachytic fabric and are associated with abundant granules of iron ore as well as epidote, occasional sphene and perhaps some needles of hornblende or pyroxene. A green to greyish granular material may be residual glass. Veins of epidote, calcite and albite sometimes occur in the more altered varieties.

The feldspar phenocrysts are idiomorphic to subidiomorphic and are tabular to prismatic in habit. They are as much as 3 mm. in length and when the composition can be determined it is albitic, becoming more calcic in the varieties which approach the andesites in composition. In these types it tends towards oligoclase and may even be andesine. Extensive alteration often masks the composition of the feldspar, the secondary minerals being albite, sericite, epidote, chlorite and some kaolin.

Hornblende is found as idiomorphic to subidiomorphic phenocrysts which have been rounded by corrosion and which usually show some alteration to epidote, chlorite, sphene, iron ore and carbonates. The size of the phenocrysts is variable, often reaching 3 mm., although the average length is less than 1 mm. They are brownish-green in colour; the pleochroism ranges through pale yellow, greenish brown and bluish-green and the extinction angle is 15° to 19° . An exception to this is found in T5 where all the phenocrysts are of brown hornblende associated with smaller phenocrysts of apatite.

The augite in T7 is fine-grained and idiomorphic to subidiomorphic. It is pale grey in colour, has an extinction angle of 46° and shows slight corrosion. Inclusions of iron ore and feldspar are present.

Andesites.

The andesitic group of lavas is distinguished from the trachyandesites by the absence of orthoclase and from the basalts and trachybasalts by the absence of augite in the groundmass. Their specific gravities range from 2.76 to 2.92, the average being about 2.83, whilst the feldspar compositions vary from andesine to labradorite. An augite hornblende andesite has been analysed (Table 2).

Hornblende Andesites. Without applying staining tests for orthoclase it is difficult to distinguish hornblende andesites from hornblende trachyandesites. The former are dark grey to greenish-grey rocks with cream or white feldspar phenocrysts associated with hornblende crystals.

In thin section the groundmass is grey and translucent with dark patches which produce a mottled appearance. Tiny feldspar laths show a tendency towards trachytic fabric and are associated with granules of sphene, epidote, chlorite, ilmenite and idiomorphic crystals of apatite. Veins and vugs of epidote, calcite and chlorite occur frequently and have produced much alteration in the rocks.

The composition of the feldspar varies from albite-oligoclase to andesine-oligoclase though alteration usually gives the feldspar crystals a greyish and speckled appearance. The alteration products are kaolin and sericite with occasional epidote and chlorite and they are often arranged zonally. In A3 the feldspar crystals consist of a core of epidote and clinozoisite sometimes with chlorite, surrounded by a clear margin of feldspar which is probably oligoclase.

The hornblende shows prismatic habit and in A3 is as much as 3 mm. in length. It is brownish-green in colour, has an extinction angle of 19° and is strongly pleochroic (greenish-yellow, brownish-yellow and grass green). Many crystals are corroded and some have released iron ore around the margins and as inclusions. Alteration is fairly well advanced, the products being epidote, chlorite and sphene as well as carbonates and ilmenite. In some rocks the

hornblende has been entirely replaced by these minerals and can be recognised only by its habit.

Augite Andesites. The augite andesites are characterised by the presence of variable amounts of glass at different stages of devitrification. A16, a pitchy black rock with felspar phenocrysts, has the most glass and also the lowest specific gravity of the augite andesites which have been examined. The others are greenish-grey in colour with tabular felspars which usually show signs of albitisation.

In thin section the groundmass is translucent to almost opaque and is brown to dirty grey in colour. Under crossed nicols microlites of felspar are sometimes visible in a matrix which shows slight double refraction. Under higher magnification this material has a rough bleb-like appearance and shows slight double refraction or it consists of pale green isotropic granules associated with tiny granules of iron ore and chloritic material. The material is thought to be due to the devitrification of a glassy matrix in the original lava.

The felspar phenocrysts are very abundant and are usually altered but in A16 they are comparatively fresh andesine. These crystals are clear and corroded and show pseudo-inclusions. Zoning is developed, the zones showing an increasing refractive index; some have the composition $Ab_{55}An_{45}$. In A17 the felspar seems to have been more basic than this and may have approached labradorite but both here and in other rocks it has been altered to sericite, kaolin and chlorite.

The augite is pale green in colour and much fresher than the felspar. It shows some corrosion and in A16 and A17 contains fine Schiller inclusions. Chloritisation has occurred, occasionally producing complete pseudomorphs. Some pseudomorphs consist of epidote, chlorite, serpentine and sphene and are intergrown with the augite. They show an octagonal cross section and may have been hypersthene. In A18 pseudomorphs of granular quartz, serpentine or chlorite, carbonates and talc assume a regular form like that of olivine.

Augite Hornblende Andesites. Intermediate between the hornblende and augite andesites are types which contain both of these ferromagnesian minerals in variable proportions. The hornblende is brownish-green when unaltered and usually of larger grainsize than the augite. In one rock it reaches 5 mm. in length while in the same rock augite is no longer than 1 mm. Corrosion has caused rounding of the phenocrysts and deposition of iron ore in the hornblende. Felspar phenocrysts have been altered to kaolin, sericite, epidote and albite.

Basalts and Trachybasalts. The basalts are characterised by the presence of large phenocrysts of augite set in a groundmass which contains granular augite. Felspar phenocrysts may, or may not be present. The specific gravities vary from 2.82 to 3.02 and the felspar composition, where determinable, is labradorite. In the case of the trachybasalts orthoclase is present in the felspar of the groundmass.

The basalts are greenish-grey, dark grey or purple in colour, according to the amount of and to the type of deuteric alteration in the rock; in nearly every case vugs filled with green, pink or white minerals are present. Large tabular crystals of pyroxene are visible and sometimes there are creamy coloured felspars as well.

In thin section the groundmass is brownish and speckled unevenly with iron ore. It consists of felspar laths with interstitial augite, carbonates, chlorite, iron ore and sphene. Epidote is present in some rocks, as is also interstitial glass. Patches of deuteric minerals are very common.

The felspar phenocrysts are idiomorphic to subidiomorphic and of tabular habit. They are rarely fresh, being altered to kaolin, sericite, chlorite, carbonates and sometimes albite. These products may be zonally arranged or may preserve,

by their orientation or distribution, the original cleavage or twinning of the crystal. In B7 a felspar crystal has been completely pseudomorphed by carbonates and chalcedony with some chlorite, the minerals being arranged in bands in a regular structure (Fig. 3H). In another basalt red and green patches in the rock seem to be due to pseudomorphs of felspar by haematite and carbonates.

The augite phenocrysts show a tendency to be glomero-porphyritic. They are light grey in colour, are idiomorphic to subidiomorphic and in B7 are as much as 4 mm. across. Colour zoning and polysynthetic twinning are developed and rounding of crystal margins and the development of pseudo-inclusions. Slight alteration to chlorite, carbonates and iron ore has occurred.

Vugs or solution cavities are numerous and contain chlorite, carbonates, epidote, zeolites and chalcedony. They vary in diameter from about 10 cm. to <2 mm. and usually show a zonal arrangement of minerals (Fig. 3).

The flow which has been called a trachybasalt has been examined in two phases in slides B11 and B12. The groundmass consists of laths of felspar and purplish augite with granules of iron ore, epidote, sphene as well as interstitial chlorite and carbonates. The presence of orthoclase in the groundmass felspar has been verified by staining tests.

The rock is grey and is set with greenish tabular felspars as much as 10 mm. in length (B11) and augite crystals which are more than 6 mm. (B12). B12 is the coarser phase of the flow and the groundmass tends to be doleritic.

The felspar phenocrysts have been zonally altered to sericite with some albite, epidote and carbonates.

(iii) Occurrence of Xenoliths.

Inclusions are plentiful in many of the lava flows, often to such an extent that the flow may be mistaken for a breccia especially when weathering is advanced. A noteworthy feature of most of these inclusions is that even though they differ from the enclosing rock in grainsize they have a similar mineralogical composition. Their contours are rounded suggesting a certain amount of resorption which gives them the appearance of water-worn boulders.

Several xenoliths have been examined in thin section and in every case they possess much coarser grainsize than the enveloping rock and are clearly defined from it. They consist of stout, interlocking felspar crystals, sometimes with plates and crystals of hornblende or augite and always with interstitial chlorite, epidote, iron ore and carbonates (Fig. 2B).

A xenolith in an augite hornblende andesite consists of large plates of green hornblende with large apatite prisms, small crystals of augite and felspar, and epidote, chlorite and carbonates with a little iron ore in the interspaces.

The crystals present in the xenoliths are usually similar in composition to the phenocrysts of the enclosing lava but this is not always so as in one of the hornblende trachyandesites a xenolith contains some augite. The xenoliths vary in size from 5 mm. by 2 mm. to several centimetres in diameter.

A. G. Macgregor (1938) has recorded from the modern volcanic region of Montserrat xenolith-bearing lavas which resemble these in habit and crystallinity. He suggests that they are "partly crystallised magma that once lined the walls of the magma conduit. During renewal of upward movement of similar magma, pieces of semi-crystallised wall rock were torn from the conduit sides, and incorporated as xenoliths in the ascending magma". The coarse grainsize and interstitial filling of deuteric material certainly suggest that the crystals were formed slowly. The interspaces may have been filled with residual material either before or after extrusion.

The incorporation of inclusions of lava, slate, dolerite, etc., as well as the cognate xenoliths in the lavas at Wellington, may be due to explosive activity preceding eruption and to the addition of talus material after extrusion.

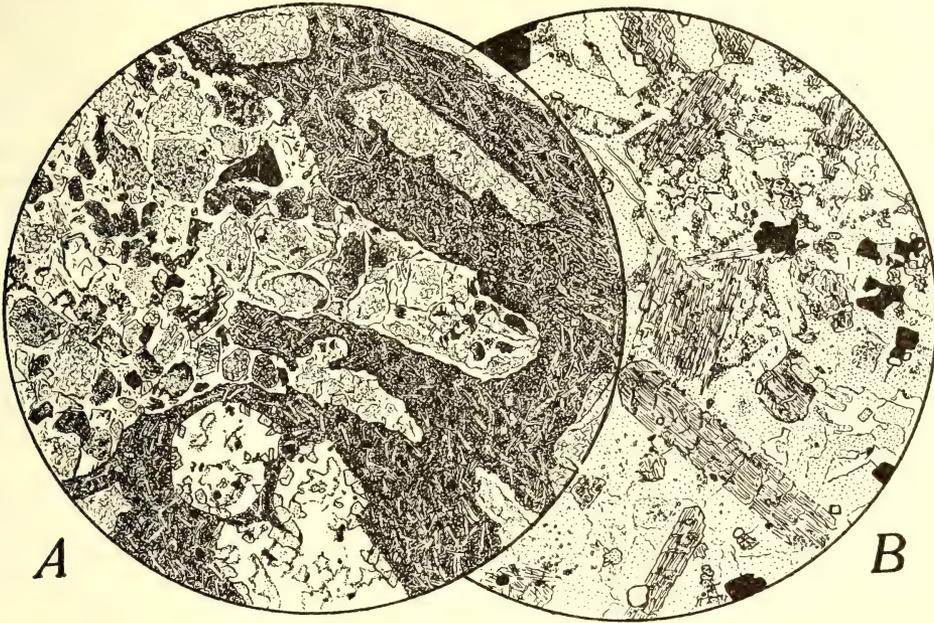


Fig. 2.

- A. A lava fragment (probably porphyritic trachybasalt) included in a tuff. The tuff shows an intrusive relationship towards the lava and consists of fragments of lava and altered primary minerals which now consist of carbonates, sericite and chlorite, set in a fine cement of the same materials. Deuteric alteration has also affected the dark coloured lava in which iron ore has been released and feldspars completely sericitised. Intrusion is apparently effected by the action of deuteric vapours. $\times 20$.
- B. Xenolith included in porphyritic hornblende andesite. The andesite has phenocrysts of hornblende and plagioclase set in a fine feldspathic groundmass and the xenolith consists of feldspar and hornblende in interlocking crystals of fairly even grainsize. Deuteric activity has affected both lava and xenolith altering hornblende to chlorite, epidote and carbonates and causing sericitisation of feldspar. $\times 20$.

4. PYROCLASTIC ROCKS.

(i) Nomenclature.

The pyroclastic rocks include extremely fine-grained tuffs, breccias and agglomerates which are formed of angular and rounded blocks measuring as much as 3 ft. by 3 ft. 6 ins. in cross section. They may be divided broadly into two groups :

Lithic tuffs, breccias and agglomerates, and
Crystal tuffs.

The former are composed mainly of lava fragments and are found interbedded with the lavas, while the crystal tuffs occur for the most part with the slates and limestones of the Upper Sedimentary series (Basnett and Colditz, 1945). The breccias which contain both lava and other fragments occur near the top of the Volcanic series.

(ii) Petrography.*Lithic Tuffs.*

In many of the lithic tuffs and breccias fragments of lavas are massed together so closely that a tuffaceous matrix is not always visible in hand specimen. Such a rock occurs in Pors. 203/101, Par. Nanima; it consists of small angular rock fragments about $\frac{1}{4}$ inch across and coloured pale green, bluish green, purple or almost black. A few small cavities filled with carbonates are present. Examination of a thin section reveals that the dark fragments have a great concentration of iron ore and that some are welded by a narrow vein of felsitic material (possibly chalcedony) whilst others are joined by tuffaceous material or are in direct contact. The tuffaceous material consists of crystal fragments of greenish-brown hornblende, colourless augite and feldspar and numerous tiny pieces of rock cemented with felsitic material. Chlorite is abundant and some carbonates are present. Where the tuff adjoins a fragment of lava there is sometimes evidence of mechanical stoping (Fig. 2A).

Other tuffs and breccias appear more homogeneous as there is less colour variation. One type cropping out in Por. 182, Par. Micketymulga is a grey aphanitic rock resembling a lava; actually it consists of fragmental feldspar, augite and hornblende crystals together with many small pieces of lava which vary in crystallinity, some being glassy and others hyalopilitic; some fragments have been impregnated with iron ore; chlorite is abundant.

The presence of rock types foreign to the lavas of the Volcanic series is not noticeable in the finer-grained rocks and it is possible that they do not occur, but in some of the coarser breccias there are pebbles of quartz dolerite, slate and other rock types. The pebbles are either rounded or angular and are as much as 3 or 4 inches in diameter.

Crystal Tuffs.

The crystal tuffs overlie the lavas for the most part and are variable in grain size. In hand specimen the fine-grained types show sub-conchoidal fracture and are medium to dark grey aphanitic or cherty rocks. Some recrystallised types are buff coloured and mottled and these may contain small rounded quartz crystals. The coarser types contain macroscopic feldspar laths in a fine groundmass.

Thin sections of the fine tuffs reveal a porphyritic grain size with small phenocrysts (up to 0.5 mm.) of albite-oligoclase and quartz embedded in a very fine-grained groundmass of similar material. A brownish, green or grey material is patchily distributed and seems to consist of chlorite, epidote and iron ore. Carbonates and micaceous material are sometimes developed.

Most of these tuffs appear to have been recrystallised as in some sections both the phenocrysts and groundmass minerals show distinctly crenulated margins. In a tuff from Por. 1, Par. Nanima, sieve-like plates of hornblende have been formed.

The coarser crystal tuffs consist of interlocking feldspar laths up to 3 mm. in length. Small quartz crystals are present as well as fibrous chlorite and epidote. The feldspars are mainly albitic but some orthoclase and oligoclase may occur.

The presence of chlorite to the exclusion of hornblende and pyroxene is an interesting feature of most of the crystal tuffs.

5. ALTERATION.

One of the most interesting facts arising from an examination of the volcanic rocks at Wellington is that almost without exception, they have suffered some degree of alteration. The presence of veins and vugs within the rocks as well

as the nature of many of the mineralogical changes make it fairly clear that most of the alteration has been caused by deuteritic activity during the period of vulcanism rather than by post-Silurian processes of weathering and metamorphism. The devitrification of the glassy groundmass of some of the augite andesites may be due either to deuteritic action or to slight regional metamorphism.

Most of the lavas, particularly the basalts, in which the mineral constituents have been intensely altered, show veins and vughs filled with deuteritic minerals. The veins are often visible in hand specimen and vughs up to 6 inches across are seen more rarely but there is ample microscopic evidence of both. The deuteritic minerals are albite, epidote, calcite, chlorite, chalcedony and zeolites and these are usually arranged zonally in the cavities. The lining of the cavity is usually of chlorite and chalcedony or more rarely epidote (Fig. 3D) the centre being filled with calcite, chlorite or zeolites. Although not identical with the deuteritic filling of the vesicular cavities in the trachybasalt at Port Kembla (Browne and White, 1928) these minerals are quite similar in composition and arrangement.

Another noticeable effect of deuteritic activity, and one readily noticed in hand specimen, is the change in colour of the lavas. The less altered types are grey to dark grey in colour but alteration has produced greenish-grey, bluish-grey, blue and purple rocks. The latter colour occurs frequently and is due to a strong introduction of iron by magmatic solutions. Comparable changes in colour due to deuteritic activity have been recorded in lavas at Blair Duguid (Browne and White, 1926) and Port Kembla (Browne and White, 1928). A fact which restricts these colour changes to the time of extrusion is that fragments of multi-coloured lavas are preserved in the lithic tuffs and breccias which are interbedded with the flows. The breccias themselves sometimes contain cavities filled with carbonates, chlorite and chalcedony but any alteration produced in the fragments after deposition of the breccia is superimposed upon a stronger and earlier alteration in the fragments.

The original mineral constituents of the lavas have suffered a considerable amount of alteration, especially the feldspar phenocrysts, which are never found absolutely unaltered and are often completely pseudomorphed even though the groundmass feldspar may have been but slightly changed. Hornblende, too, is much altered, while augite often remains quite fresh. In general, the groundmass is less altered than the phenocrysts even though the products of alteration are similar.

The alteration products of the feldspars are often arranged in zones or they may preserve some other mineral structure such as cleavage or twinning. They consist of albite, sericite, epidote, chlorite, carbonates and kaolin; of these albite is found most frequently as the replacing mineral in the trachyandesites while in the basalts mica and carbonates are strongly developed. The chemical analyses show an increase in the proportion of K_2O to Na_2O in the basaltic type and this is probably due to the presence of sericite. In one porphyritic basalt the feldspar has been completely pseudomorphed by haematite and carbonates.

The most noticeable change in the hornblende phenocrysts is the development of fine granules of iron ore around the borders of the crystals. This process is sometimes sufficiently advanced to produce complete pseudomorphs and is due to resorption rather than to deuteritic action. Macgregor has recorded similar resorption of hornblende in the lavas at Montserrat (1938). Some deuteritic alteration occurs along cleavage and cracks in the crystal forming epidote, chlorite, sphene, iron ore and carbonates.

Chloritisation of augite sometimes occurs and in the basalts carbonates and iron ore also occur as alteration products. The relative freshness of augite in otherwise much altered rocks has been recorded from Maitland (Browne,

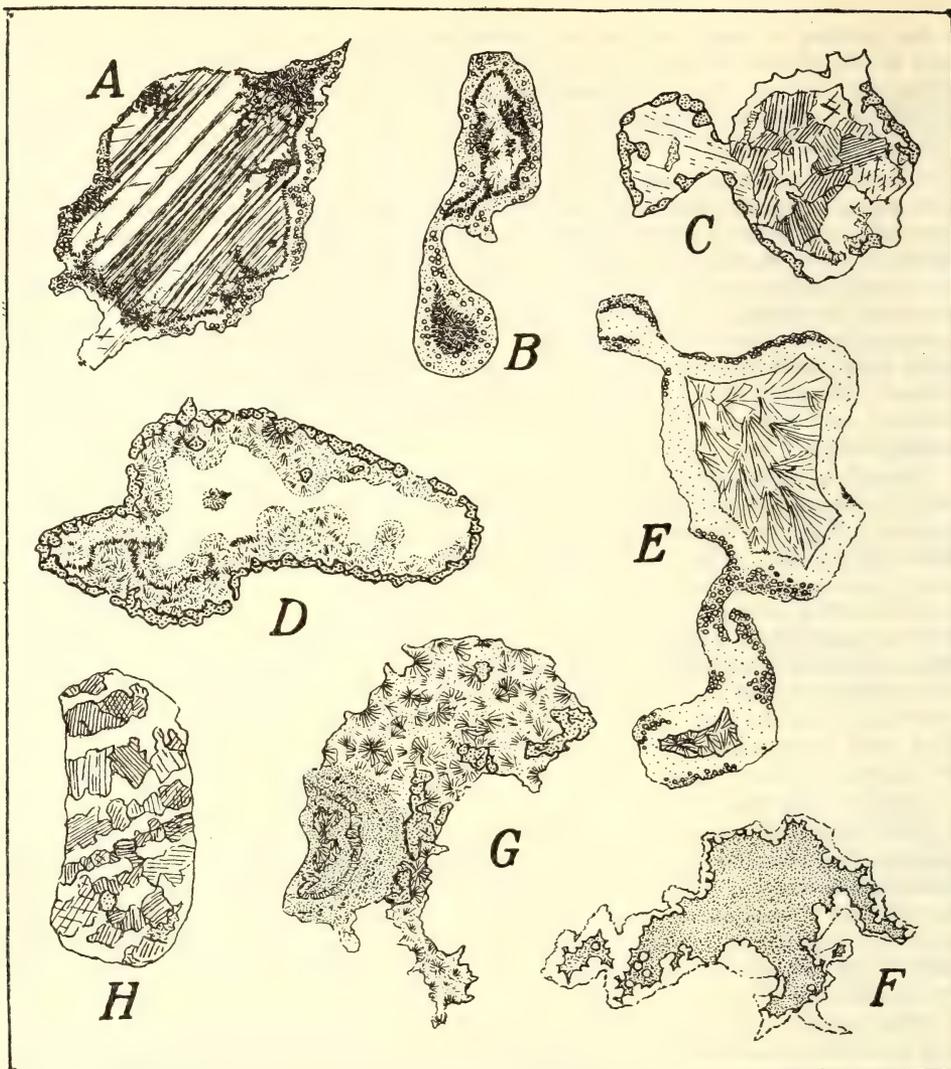


Fig. 3. Evidences of Deuteric Activity in the Lavas. $\times 16$.

- A. Slide A22. This vugh has a discontinuous lining of pale green chlorite followed by a narrow zone of carbonates, both minerals containing globules of chalcidony. Next comes an irregular layer of fibrous blue-green chlorite and the centre is filled with carbonates.
- B. Slide A22. This cavity is almost completely filled with chlorite. The lining is pale green and almost isotropic with globules of chalcidony. Within this is a narrow zone of larger bluish-green fibrous crystals while the central portion contains a paler fibrous chlorite.
- C. Slide B8. A few grains of epidote and an occasional patch of chlorite form the outer layer of this vugh, which is followed by a discontinuous zone of chalcidony and an infilling of carbonate.
- D. Slide B8. Epidote is developed here as an almost continuous outer layer, followed by a wide irregular zone of pale green fibrous chlorite and a centre of chalcidony.
- E. Slide A10a. Chlorite with chalcidony globules is sparsely developed around the walls of the vugh and the interior consists of fine fibrous zeolite bounding a central region with coarser crystals.
- F. Slide B7. The walls of this cavity are lined with chalcidony, which shows a botryoidal surface against the infilling chlorite.
- G. Slide B1. Pale green fibrous chlorite with a few grains of epidote compose the greater part of this vugh, but in the lower portion of the diagram layers of chalcidony and chlorite are zonally arranged.
- H. Slide B7. The pseudomorph of a felspar crystal in which granular carbonates and chalcidony with some chlorite are arranged in regular bands.

1922) and from Prospect (Browne, 1924). In the analcite dolerite at Prospect the only alteration is to chlorite with occasional calcite as is found at Wellington.

In the vicinity of the Bodangora gold mines and to the south-west of Apsley railway station the rocks have been intensely altered either by deuteric action, by quartz veins from the Wuuluman granite, or by both. At the former locality the thin section of an andesite shows almost complete obliteration of previous rock structures as alteration to carbonates and mica is practically complete. There is some chlorite and kaolin and a few granules of feldspar remain in the ghosts of former feldspar phenocrysts. Near Apsley there is evidence of strong introduction of iron ore by deuteric solutions; it forms a dense deposit in granules around vugs and cracks in the rock. Another flow which is from Por. 267, Par. Wellington, and is an altered porphyritic basalt has its augite phenocrysts partly replaced by quartz and copper while the remainder of the rock has been pseudomorphed by epidote and quartz.

About 2½ miles south-west of Bodangora a few lava flows come into contact with the Wuuluman granite. In these the groundmass has been completely recrystallised to feldspar granules and fibrous green hornblende which is arranged in parallel groups. The feldspar phenocrysts show partial recrystallisation around the edges and the inclusions have formed tiny fibres of green hornblende.

6. PETROGENESIS.

(i) Chemical Discussion.

It is not a simple matter to interpret the petrology of this group of lavas, as no definite sequence of extrusion has been observed over a large area. This fact is not surprising when one considers the complexity of present-day volcanic regions where there is much overlapping of flows from different vents, where lavas merge into agglomerates and where a great deal of contemporaneous erosion and earth movement takes place. The Wellington lavas must have been laid down under conditions similar to these and they have been faulted and folded since their deposition.

Three volcanic rocks and three hypabyssal types have been analysed covering a range of 17% SiO₂ (Table II). The analysed lavas have a range of 12% SiO₂ and as they are fairly normal types of trachyandesite, andesite and basalt this should approach the complete silica range of the Wellington lavas.

The analysis of the porphyritic basalt shows a near relationship to "hessose" of the C.I.P.W. classification, augite hornblende andesite resembles "andose" and hornblende trachyandesite is comparable with "pulaskose".

In the norms of the three lavas (Table IIIA) there is a noticeable increase in normative orthoclase in the trachyandesite and the plagioclase feldspar shows a pronounced increase in the proportion of albite to anorthite.

Mineralogically the basalts appear to be of the tholeiitic magma of Kennedy (1933), since they contain pyroxene to the exclusion of olivine. Chemically, however, the analyses are not similar to his except in the silica percentage; also the line of descent for the tholeiitic magma (viz. tholeiitic basalt → andesite → rhyolite) is contradicted at Wellington by the presence of the trachyandesites which Kennedy places in the olivine basalt sequence.

The group of lamprophyre sills to the north-east of Wellington appear to be related to the lava series as they show close affinities to them both in appearance and in field occurrence (Basnett, 1942; Basnett and Colditz, 1945). Analyses of three of them, together with the three lavas, have been plotted on a variation diagram which is figured below (Fig. 4). These rocks have been referred to as augite lamprophyres throughout the text but are listed as amphibolites in Table II. This is due to the fact that the augite has in most cases been altered to amphibole by contact metamorphism, a change which is obvious only in thin section.

Since analyses are so few and as there have been deuterio changes in the lavas the chemical relations must be somewhat conjectural, but despite this the diagram has some features of interest.

A specific gravity curve has been superimposed and shows a good deal of conformity with the amount of lime and magnesia present in the rocks.

TABLE II.
Table of Analyses.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO ₂	45.49	47.52	49.24	50.46	56.65	62.55	50.85	50.71
Al ₂ O ₃	10.49	12.50	13.85	17.99	20.37	17.46	16.07	17.92
Fe ₂ O ₃	6.44	1.08	4.88	1.06	1.24	2.37	4.58	5.14
FeO	4.36	6.26	6.55	5.76	3.28	2.03	6.45	4.73
MgO	18.48	16.50	8.34	6.78	3.20	1.43	4.23	4.67
CaO	10.72	13.07	10.94	10.91	4.31	2.55	7.83	7.28
Na ₂ O	0.89	0.46	2.55	0.97	5.65	4.99	2.57	2.49
K ₂ O	1.25	0.92	1.32	1.63	2.75	4.78	2.03	2.16
H ₂ O+	1.55	0.85	0.72	2.38	1.43	0.85	2.41	1.96
H ₂ O-	0.11	—	0.16	0.04	0.11	0.08	0.16	0.62
TiO ₂	0.36	0.67	0.62	0.88	0.67	0.52	1.30	1.04
P ₂ O ₅	0.24	tr.	0.31	0.29	0.29	tr.	0.33	0.35
MnO	0.15	0.14	0.17	0.12	0.08	0.44	0.09	0.09
CO ₂	—	—	—	1.12	—	—	0.79	0.48
Total	100.53	99.97	99.65	100.39	100.03	100.05	99.69	99.64
Sp. Gr.	3.10	3.13	3.09	2.92	2.77	2.74	2.92	2.80

- I. Spinel Amphibolite. Por. 14, Par. Bodangora. Anal. E. M. Basnett.
 II. Epidote Amphibolite. Por. 83, Par. Bodangora. Anal. M. J. Colditz.
 III. Felspar-bearing Amphibolite. Wuuluman Road Crossing of Pogygy Creek. Anal. E. M. Basnett.
 IV. Porphyritic Basalt. Por. 93, Par. Nanima. Anal. M. J. Colditz.
 V. Augite Hornblende Andesite. Por. 251, Par. Micketymulga. Anal. M. J. Colditz.
 VI. Hornblende Trachyandesite. Por. 94, Par. Nanima. Anal. M. J. Colditz.
 VII. Augite Porphyrite. Por. 145, Par. Copper Hill, Molong. Anal. R. Brewer.
 VIII. Augite Andesite. Por. 1, Par. Bell, Molong. Anal. D. Moye.

TABLE IIA.
Norms.

	IV.	V.	VI.
Quartz	6.36	—	7.32
Orthoclase	9.45	16.68	28.36
Albite	8.38	48.21	42.44
Anorthite	39.75	19.74	11.12
Corundum	—	0.71	—
Diopside	4.48	—	1.33
Hypersthene	23.19	2.39	3.89
Olivine	—	6.93	—
Magnetite	1.86	1.86	3.48
Ilmenite	1.67	1.37	0.91
Apatite	0.67	0.67	—

At the basic end of the series magnesia is dominant and is associated with high lime and iron, a moderate amount of alumina and low alkalis. This composition is expressed mineralogically by the dominance of augite (altered to amphibole) in the most basic rocks where felspar is rare. With increasing

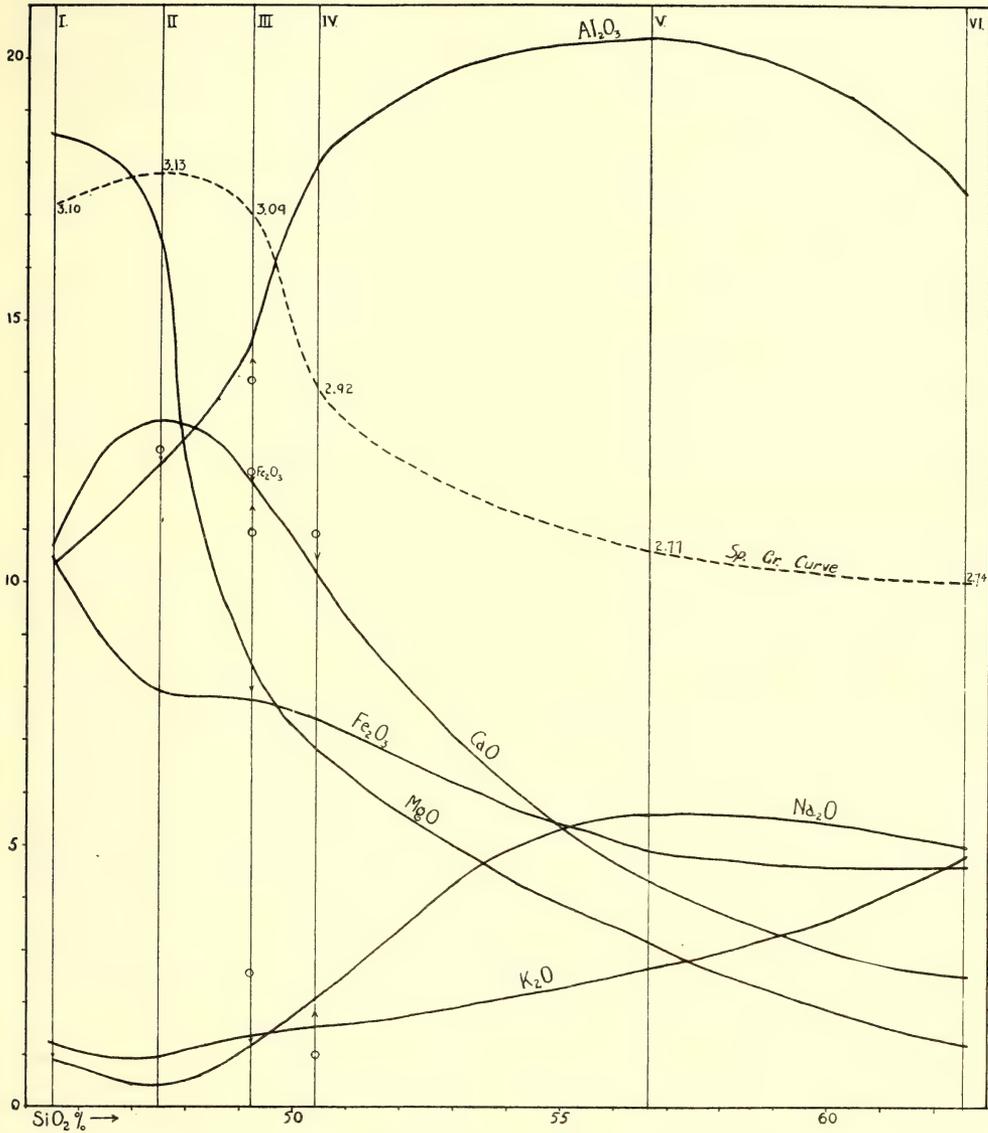


Fig. 4. A Variation Diagram of the Lava Series and Lamprophyres. For analyses and names of rocks, see Table II.

silica plagioclase becomes more abundant and the increase in lime involved in its formation is shown by the steep rise in this curve between analyses 1 and 2; this is accompanied by a rise in alumina and a fall in magnesia and iron.

The lavas are joined by more gentle curves which show decreasing lime, magnesia and iron and increasing alkalis. With the formation of anorthite the

alumina curve rises, but as the plagioclase becomes albitic and hornblende develops the soda and alumina curves reach a maximum and then fall towards hornblende trachyandesite.

The potash in the basalt is probably contained in the sericite alteration product of the plagioclase. There is a very pronounced increase in soda in the augite hornblende andesite due to an increase in the proportion of albite in the plagioclase and perhaps also to more albitisation of the felspar. In the trachyandesite the development of orthoclase is indicated by a rise in the potash curve and a very slight fall in soda. In these rock types the process of albitisation is more important than that of sericitisation.

The variation diagram and specific gravity curve indicate that the lavas and lamprophyres form a volcanic suite in which an increase in silica percentage involves a decrease in specific gravity and an increase in the albite molecule of the felspar.

A graph in which the silica percentages of the lavas have been plotted against their specific gravities suggests the range of silica for the rock types. On this diagram an average of the three analysed amphibolites has been used to represent the lamprophyres. The range of specific gravities of the lavas has been obtained from Table I and exceptional values have not been considered as they are probably due to excessive alteration. The silica percentages of the lamprophyres are seen to vary from 45 to 49, the basalts from 49 to 50.5, the andesites from 50.5 to 58, and the trachyandesites have more than 56.5% SiO_2 .

(ii) Magmatic History.

A comparison of the mineralogy of the Wellington lavas and lamprophyres as well as a study of their analyses suggests that the differences in composition of lavas and sills can most easily be accounted for by the sinking of crystals in a magma reservoir as formulated by Bowen (1928).

The original composition of the magma in the reservoir was probably andesitic and intermediate between analyses IV and V (*vide* Table II and Fig. 5), with a silica percentage of about 54. In discussing the origin of the Garabal Hill-Glen Fyne complex and also the volcanic rocks of Lower Old Red Sandstone age (Nockolds, 1941), is of the opinion that the parent magma had the composition of a pyroxene-mica diorite or a pyroxene andesite. The analyses which he gives are intermediate in composition between the augite hornblende andesite and the porphyritic basalt at Wellington. This magma, then, must have been very like that which produced the volcanic sequence at Wellington.

The crystallisation of augite and felspar was followed by the extrusion of augite andesites and porphyritic basalts. A period of quiescence was accompanied by sinking of the augite due to its high density and subsequent formation of hornblende. This allowed for the extrusion of hornblendic types as well as lavas containing both hornblende and augite.

The presence of microphenocrysts of apatite in the hornblende andesites, as well as very abundant alkalis, bears out the idea that this lava type may have formed one of the upper layers in the magma reservoir together with the trachyandesites.

With a fresh influx of material or a mixing of the residual magma a repetition of the process would occur, except that in the latter case more basic types would be formed.

Bowen's theory could also explain the occurrence of augite andesites and porphyritic basalts with different proportions of augite and felspar phenocrysts, since in the zone where augite was most abundant felspar would be least abundant. The augite lamprophyre is the extreme case where no felspar phenocrysts are present and the residual magma with its large crowded augite

crystals was intruded as lenses in the soft sediments at the close of, or during, Silurian time.

During the earlier stages of volcanic activity lavas were poured out and intermittent explosive action caused the formation of beds of pyroclastic material. The centres of eruption were situated close to the sea and lenses of limestone were formed when conditions remained stable for a sufficiently long period. At the close of the period of vulcanism explosive action increased in frequency as indicated by an increase in breccias, tuffs and agglomerates ; these were succeeded in more peaceful times by tuffaceous sediments in which the tuff may have been derived from distant sources.

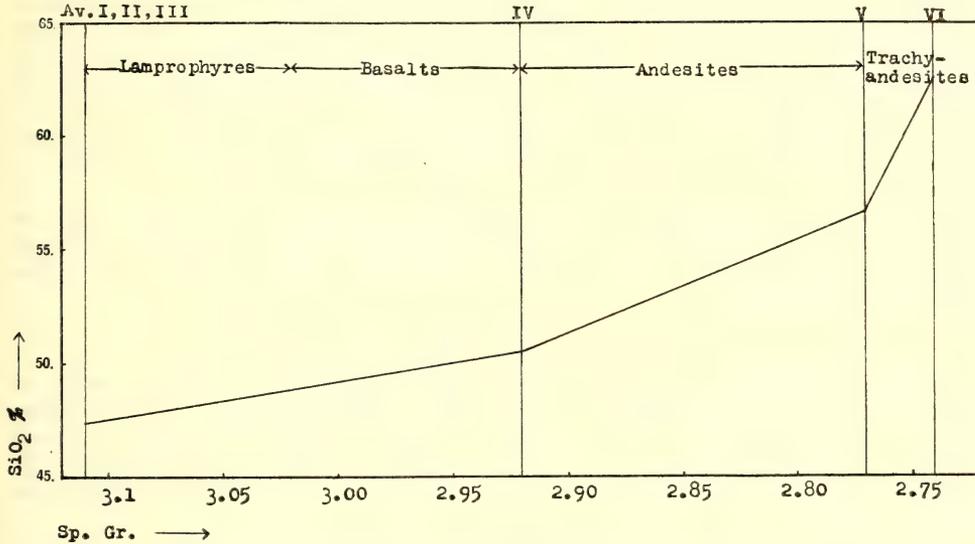


Fig. 5. Diagram showing the Range of Silica Percentages and Specific Gravities.

The lavas were probably extruded from several different vents as the flows are not persistent over any great area but all show certain phenomena in common such as deuteric alteration and xenoliths. The flows were all porphyritic but varied in the amount of glass present, some having an entirely glassy matrix and others being quite free from glass. Many hornblendic types had their phenocrysts resorbed due to decrease of temperature and pressure during ejection and were left with "ghost" phenocrysts of iron ore. Magma often began to crystallise within the vent but when eruption took place the crystals were torn from the walls and included as cognate xenoliths in the lava. Other xenoliths, mainly of lava, would be gathered up from talus material lying in the path of the flow.

In some cases deuteric alteration probably commenced while the lava was still pouring from the vent and continued until the flow was quite cool. The remaining volatiles became segregated in the vesicles near the surface of the flow and crystallised there.

Intermittent explosive action produced fragmentation of the lavas and their phenocrysts and sometimes included rocks foreign to the area ; this was especially so when explosive activity was dominant.

7. COMPARISON WITH OTHER AREAS.

The volcanic rocks of the Wellington district can be traced southwards to Molong, where they have been examined by R. Brewer, B.Sc., and D. Moye,

B.Sc. Two analyses from Molong have been included in Table II. The extent of the lavas, from the Jurassic rocks near Geurie, southwards through Wellington and Molong to the Orange district, is a distance of about 70 miles.

At Cargo, to the south-west of Orange, Andrews has recorded andesites, trachytes, dolerites and pitchstones, interbedded with breccias and tuffs and associated with Silurian sediments (1915). He also describes (1910) augite andesites banded with slates and tuffs in the Forbes-Parkes district which lies to the south-west of Wellington.

To the south-east of Orange, augite andesites similar to those at Wellington have been described by Whitworth at Blayney (1938) and Harper (1920) recorded both augite andesite and serpentine from Lucknow. The latter occurs in lenses and is intrusive; its correlation with the augite lamprophyre is quite possible.

These Silurian volcanic rocks, many of which are auriferous, show petrographical affinities to one another and form part of a petrographical province which occupied the central part of the state during the Silurian period (Browne, 1929). That it had rather alkaline affinities is supported by the fact that there are moderately high alkalis in the analysed rocks from Wellington and Molong (Table II).

The complex nature of the Wellington lavas with their overlapping xenolithic flows, resorbed hornblende crystals and interbedded tuffs and limestones is not unlike the volcanic island of Montserrat, where recently formed lavas show similar characteristics.

8. SUMMARY.

To the east and north-east of the town of Wellington, N.S.W., a series of volcanic and interbedded pyroclastic rocks is exposed. The volcanic series extends from Geurie to Wellington and southwards to Molong and Orange, although only the Wellington area is discussed. It can be correlated with andesites at Blayney and Lucknow and with similar rock types in the Forbes-Parkes district.

Lava types examined petrographically have been classed as trachyandesites, andesites, basalts and trachybasalts and these show genetic relations with sills of augite lamprophyre which occur about 10 miles east of Wellington and which are intruded into the Silurian strata.

A feature of the lavas is their widespread alteration and the presence of many veins and vughs which are attributed to deuteric activity during extrusion. The lavas are interbedded with tuffs, breccias and agglomerates which are for the most part closely related to the lava types. Cognate and other xenoliths occur frequently in the flows.

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STUDIES IN THE INHERITANCE OF RESISTANCE TO RUST OF BARLEY.

PART II.

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INTRODUCTION.

In an earlier paper in these *Proceedings* (Waterhouse, 1927), results from several crosses between barley varieties were presented which showed that a single dominant genetic factor determined resistance to *Puccinia anomala* Rostr., the cause of barley leaf rust. There was no evidence of linkage with factors determining certain morphological characters studied.

Although much genetical work on barley has since been reported, there are apparently no records of other work on inheritance of rust resistance. The work now presented deals with a continuation of the original studies and carried forward between the years 1924 and 1941. An extensive programme of work had been planned. It later became impossible to carry it through to completion, and as it is now not intended to continue the barley work, it seems wise to make the results obtained available to other workers.

MATERIALS AND METHODS.

With a few additions, the barley varieties already classified for resistance (Waterhouse, 1927) were used. Pots of seedlings were inoculated in the usual way and the rust reactions in the plant house determined on the scale generally adopted. Parent varieties were used for direct comparison with the cross-bred material sown at the same time and kept under comparable conditions. This is necessary because alterations in the environmental conditions change the reactions shown in certain cases; this applies particularly to the group of barleys classified as being "moderately resistant" to *P. anomala*. Reactions recorded in May as "2" change to "4" in February, when much higher temperatures prevail: intermediate reactions like "2+", "X" and "4^c" are shown under intermediate conditions of light and temperature. Many of the "resistant" varieties exhibited no such variation, remaining resistant and showing "O" (flecks) under all the temperature conditions tested.

Crosses were made in the field. F1 plants after being tested in pots in the plant house were transplanted to open plots and grown to maturity. The same was done with the back-cross and certain of the F2 plants used in the F3 tests; others of these were grown from grain sown directly in the open—not tested as F2 individuals.

The culture of *P. anomala* used was the same as that reported upon previously. During the period, nine cultures derived from a number of sources were tested on an empirically selected group of "moderately resistant" and "resistant" varieties, but no departure from the behaviour shown by the stock culture was found. At the time, the set of differential varieties worked out by D'Oliveira had not been obtained.

For the stem rust tests, the standard cultures maintained for the wheat rust work were used on the barleys.

EXPERIMENTAL RESULTS.

(a) Tests with *P. anomala*.

F1 Results.

1. Crosses were made between two susceptible parents as follows :

Parents.		No. of Seedlings Tested.
Kinver	× Pryor	23
"	× Cape	10
"	× Skinless	14
"	× Trabut	2
Cape	× Kinver	4
"	× Skinless	13
"	× C.I. 2329	3
"	× Peatland	14
Skinless	× Success	11
"	× Bel. 2071	5
Volga	× <i>Hordeum spontaneum</i>	9
"	× Reka	7
Reka	× Volga	6
C.I. 2309	× C.I. 2222	23
"	× Cape	8
Golden Grain	× Mariout	3
Luth	× C.I. 2237	16

In all cases the F1 plants were susceptible ; no difference between their reactions and those of the parents could be detected.

2. One cross between two "moderately resistant" parents was made.

Minn. II 20.10B × Minn. II 21.14 gave seedlings showing a "2+" reaction similar to that of the parents tested at the same time.

3. Crosses between two "resistant" parents were made as follows :

Parents.		No. of Seedlings Tested.
Minn. II 21.15	× O.A.C. 21	12
"	× Manchuria	12
Minn. II 21.17	× O.A.C. 21	31
"	× Manchuria	15
Manchuria	× Minn. II 21.17	19
"	× Virginia Hooded	5
O.A.C. 21	× Manchuria	18
"	× Virginia Hooded	2
Virginia Hooded	× Manchuria	6

The reactions of the parents showed variations from "0" (flecks) to "1" reactions within the same pot. No differences of any significance were shown by the F1 plants.

4. Crosses between a "resistant" and a "moderately resistant" parent were made as follows :

Parents.		No. of Seedlings Tested.
Minn. II 21.15	× Minn. II 21.14	15
Minn. II 21.14	× Minn. II 21.15	15
O.A.C. 21	× California Feed	27
Virginia Hooded	× Success	1

In these cases the F1 reactions were not significantly different from the "0" to "1" reactions of the resistant parent.

5. Crosses between a susceptible and a "moderately resistant" parent were made as follows :

Parents.		No. of Seedlings Tested.
Cape	× California Feed	15
Skinless	× "	12
Kinver	× "	23
Minn. II 20.10B	× Kinver	23
"	× Minn. II 21.14	4
Minn. II 21.14	× Kinver	10
Marionet	× Skinless	15
Minn. I 16.13	× Kinver	15
Coast	× "	14
Sahara 3770	× "	24
Loeride	× "	11
Psaknon	× "	16
Orge Fourragère	× "	13

The F1 reactions were of the "2+" type, being practically the same as those of the "moderately resistant" parents. These, as pointed out earlier, give reactions that are subject to considerable variation with temperature change: in mid-summer the reaction has to be classed as "4". In a few cases F1 tests were made under these conditions, and then the reactions were also of the "4" type.

6. Crosses between a susceptible and a "resistant" parent were made as follows :

Parents.		No. of Seedlings Tested.
Minn. II 21.15	× Skinless	10
"	× Cape	9
Cape	× Minn. II 21.15	12
Minn. II 21.17	× Skinless	30
Skinless	× Minn. II 21.17	11
C.I. 2208	× C.I. 2209	10
"	× C.I. 2237	19
"	× Skinless	25
Skinless	× C.I. 2208	26
C.I. 2220	× Skinless	8
Skinless	× C.I. 2220	6
C.I. 2220	× C.I. 2222	12
Manchuria Sel. C163	× Skinless	14
Skinless	× Manchuria Sel. C163	35
Manchuria Sel. C163	× Cape	30
"	× Manchuria Sel. C225	15
"	× Kinver	19
"	× Manchuria Sel. C81	13
O.A.C. 21	× Skinless	50
Skinless	× O.A.C. 21	28
O.A.C. 21	× Cape	45
Virginia Hooded	× Volga	27
Volga	× Virginia Hooded	5
Virginia Hooded	× Luth	46
"	× Intermediate	43
"	× Weider	14
"	× Bel. 2071	13
Colsess	× Skinless	29
Manchuria	× Pryor	28
"	× Cape	19
Manchuria Sel. C168	× "	3
No. 22	× "	17
Minn. II 21.18	× Pusa No. 1	5
Bolivia	× Cape	12
Weider	× Skinless	9
Skinless	× Weider	11

The reaction of the "resistant" parents varied from "0" to "1" and was hardly distinguishable, if at all, from those shown by the F1 plants.

Summary of the F1 Results.

The evidence shows that there is dominance of resistance to *P. anomala*. This applies to the "resistant", as well as the "moderately resistant" varieties from whatever source.

Back-cross Results.

1. A back-cross between Skinless and the F1 of (Skinless × Manchuria Sel. C163) gave a total of 12 plants resistant, showing reactions "0" to "1" and 11 plants susceptible, showing "4" reactions. Progenies of only 5 of these plants were available for further tests. Three from susceptible parents gave a total of 258 tested plants, all of which were susceptible. The other 2 came from resistant plants; one gave 34 resistant and 14 susceptible plants and the other 36 resistant and 12 susceptible plants.

2. Skinless × (Skinless × O.A.C. 21) yielded 17 resistant and 23 susceptible seedlings.

3. Pryor × (Pryor × Manchuria) gave 6 resistant and 7 susceptible plants.

4. Minn. II 21.14 × (Minn. II 21.14 × Minn. II 21.15) gave 4 resistant and 5 susceptible plants.

The numbers of individuals dealt with are small, but the results point to a single dominant factor for resistance operating.

*F2 Results.**1. Crosses between Two Resistant Parents.*

(a) A cross between O.A.C. 21 and Minn. II 21.17 gave 208 plants classified as "0" to "1", these being similar to the reactions of each parent.

(b) The cross Manchurian × Minn. II 21.17 yielded 224 resistant seedlings classified as "0" to "1", similar to the parent reactions.

(c) The cross Manchurian × O.A.C. 21 yielded 245 resistant plants similar in resistance to the parents.

2. Crosses between "Resistant" and "Moderately Resistant" Parents.

The results may be summarized in the following table:

Parents and Their Reactions.	Counts of F2 Plants.				Deviation from 3 : 1 Ratio.
	Re-sistant.	Re-action.	Moderately Resistant.	Re-action.	
Californian Feed, "2+" × O.A.C. 21, "0" to "1".	157	"0" to "1"	55	"2+" to "X"	2
Minn. II 21.14, "4 ^e " × Minn. II 21.15, "0" to "X".	171	"0" to "X"	61	"4 ^e "	3
Minn. II 21.15, "0" to "X-" × Minn. II 21.14, "4 ^e ".	149	"0" to "X-"	48	"4 ^e "	1
Minn. II 21.14, "4 ^e " × Manchuria, "0" to "X-".	196	"0" to "X-"	67	"4 ^e "	1
Cape, "2+" × O.A.C. 21, "0" to "1".	142	"0" to "1"	40	"2+"	5
Minn. II 21.15 "0" to "1" × Cape "2+".	72	"0" to "1"	18	"2+"	5
Cape, "2+" × Manchuria Sel. C163 "0" to "1".	137	"0" to "1"	37	"2+"	6

The results show the operation of a single dominant factor determining "resistance".

3. Crosses between "Moderately Resistant" and Susceptible Parents.

The results may be summarized as follows :

Parents and Their Reactions.	Counts of Plants.				Deviation from 3 : 1 Ratio.
	Moderately Resistant.	Re-action.	Sus-ceptible.	Re-action.	
Cape, "4" × Californian Feed, "X"	165	"X"	52	"4"	2
Kinver, "4" × Californian Feed, "X"	67	"X"	19	4	2
Kinver, "4" × Minn. II 21.14, "X+"	111	"X+"	35	4	2
Kinver, "4" × Marionet, "X"	83	"X"	34	4	5
Kinver, "4" × Sahara 3770, "X"	174	"X"	66	4	6
Kinver, "4" × Psaknon, "X"	52	"X"	18	4	1

The results show the operation of a single dominant factor determining "moderate resistance".

4. Crosses between "Resistant" and Susceptible Parents.

The results may be summarized as follows :

Parents and Their Reactions.	Counts of F2 Seedlings.				Deviation from 3 : 1 Ratio.
	Re-sistant.	Re-action.	Sus-ceptible.	Re-action.	
Skinless, "4" × Minn. II 21.15, "0" to "1"	173	"0" to "1"	54	4	3
Minn. II 21.15, "0" to "1" × Skinless "4"	137	"0" to "1"	44	4	1
Skinless, "4" × Minn. II 21.17, "0" to "1"	313	"0" to "1"	120	4	12
Skinless, "4" × C.I. 2208, "0" to "1"	158	"0" to "1"	65	4	9
C.I. 2208, "0" to "1" × Skinless "4"	149	"0" to "1"	59	4	7
Skinless, "4" × C.I. 2220, "0" to "1"	22	"0" to "1"	7	4	—
Skinless "4" × Manchuria Sel. C163, "0" to "1"	182	"0" to "1"	62	4	1
Manchuria Sel. C163, "0" to "1" × Skinless "4"	239	"0" to "1"	78	4	1
O.A.C. 21, "0" to "1" × Skinless "4"	208	"0" to "1"	82	4	9
Cape, "4" × Minn. II 21.15, "0" to "1"	26	"0" to "1"	14	4	4
Cape, "4" × O.A.C. 21, "0" to "1"	194	"0" to "1"	47	4	13
Kinver, "4" × Manchuria Sel. C163, "0" to "1"	63	"0" to "1"	19	4	2
Totals	1,864		651		22

In all cases the deviation from the expectancy for a 3 : 1 ratio is less than twice the S.E. The results show the operation of a single dominant factor for resistance.

In three of the crosses, the F₂ plants after testing were grown to maturity and their morphological characters determined in regard to beard, hulled grain and smooth awn. Rust resistance was inherited independently of any of these features.

F₃ Results.

Progenies of three of the crosses studied in the F₂ were examined with the following results :

Parents of Cross.	Classification of F ₃ Families.					
	Homo-zygous Re-sistant.	Average No. of Plants Tested.	Hetero-zygous Re-sistant.	Average No. of Plants Tested.	Homo-zygous Sus-ceptible.	Average No. of Plants Tested.
(a) Skinless × Minn. II						
21.15	56	26	98	24	52	19
Expectancy ..	51.5		103		51.5	
(b) Cape × Minn. II						
21.15	6	20	21	27	10	25
Expectancy ..	13.25		26.5		13.25	
(c) Skinless × Minn. II						
21.17	20	29	40	25	27	31
Expectancy ..	21.75		43.5		21.75	

Summation of Individuals in the Heterozygous F₃ Families.

Parents of Cross.	Resistant.	Susceptible.	Deviation from 3 : 1 Ratio.
Skinless × Minn. II 21.15	1,802	612	8
Cape × Minn. II 21.15	409	160	18
Skinless × Minn. II 21.17	759	248	4
Total	2,970	1,020	22

In all cases the deviation from the expectancy on a 3 : 1 basis is less than twice the S.E.

Again there is clear evidence of the operation of a single dominant factor for resistance.

Summary of Leaf Rust Results.

The evidence from the F₁, back-cross, F₂ and F₃ results points clearly to resistance depending upon a single dominant gene. The crosses used involved parents from widely scattered areas. There is nothing in the evidence to show that it is not the same gene in the many varieties used. Additional crosses

between resistant sorts would be necessary to complete the evidence. This barley leaf rust result is entirely different from that obtained in the wheat leaf rust studies (unpublished data) where at least two major genes operate.

(b) *Tests with Puccinia graminis tritici.*

Seedling tests in the plant house do not give anything like the clear-cut reactions that are obtained with *P. anomala*; varieties which are quite susceptible show a considerable amount of chlorosis; this is general. The pustule size is the chief distinguishing feature. Again, temperature changes bring about marked alterations in the reactions. Thus a "2" in winter may increase to a "2±" reaction in summer; the latter pustule is quite a large one with considerable uredospore formation on the chlorotic areas.

Varieties were classified on the basis of their reactions to the three races of *P. graminis tritici* numbered 34, 43 and 45, as well as to *P. anomala*. Under the conditions prevailing at the time of the test, some varieties gave only "1=" reactions; the reaction "2" was taken as setting the upper limit to the resistant class. It was sometimes difficult to determine whether a "2" reaction was significantly different from a "2+" reaction which was taken as the lower limit in the susceptible class.

Based on such "resistance" and "susceptibility", 13 of the 16 possible groupings were found, as follows:

1. *Resistant to P. anomala and P. graminis tritici races 34, 43, 45.*
Virginia Hooded, Coast.
2. *Susceptible to P. anomala and P. graminis tritici races 34, 43, 45.*
Luth, C.I. 2222, Trabut, Mariout, Volga, Standwell, Hero, Intermediate, Pearl, Chedret, Coutsopodi, Janina, Sahara 3764, Sahara 3765, Burton's Malting.
3. *Resistant to P. anomala and Susceptible to P. graminis tritici races 34, 43, 45.*
Minn. II 21.15, Minn. II 21.17, Manchuria Sel. C168, Manchuria Minn. 184, Manchurian, O.A.C. 21, No. 22, Orge 4th.
4. *Susceptible to P. anomala and Resistant to P. graminis tritici races 34, 43, 45.*
C.I. 2256, C.I. 2269, C.I. 2209, C.I. 2210, C.I. 2237, C.I. 2280, C.I. 2226, C.I. 2228, Manchuria Sel. C225, Cape, Kinver, Golden Grain, Albert, Princess, Goldthorpe, Tunis, Gatama, Roseworthy Oregon, Squarehead.
5. *Resistant to P. anomala and P. graminis tritici 34 and 45, and Susceptible to P. graminis tritici 34.*
C.I. 2220.
6. *Resistant to P. anomala, P. graminis tritici 43, 45 and Susceptible to P. graminis tritici 34.*
C.I. 2208, Manchuria Sel. C163, Colsess, Orge Fourragère.
7. *Resistant to P. anomala and P. graminis tritici 45 and Susceptible to P. graminis tritici 34, 43.*
Minn. II 21.18, No. 305, Orge 14J.
8. *Susceptible to P. anomala and P. graminis tritici 34 and Resistant to P. graminis tritici 43, 45.*
Black Russian, C.I. 2206, Nepal, C.I. 2254, Gold, Salonika, Sahara 3766, Sahara 3768, Gisborne, Tennessee Winter, Hanchen.
9. *Susceptible to P. anomala and P. graminis tritici 43 and Resistant to P. graminis tritici 34 and 45.*
C.I. 2213, C.I. 2215, C.I. 2217, Zea.
10. *Susceptible to P. anomala and P. graminis tritici 45 and Resistant to P. graminis tritici 34, 43.*
C.I. 2229, Nodding Barley.

11. *Susceptible to P. anomala and P. graminis tritici 34, 43 and Resistant to P. graminis tritici 45.*
C.I. 2204, C.I. 2214, C.I. 2219, C.I. 2221, Manchuria Sel. C81, Skinless, Pryor, Reka, *H. spontaneum*, Purple Hull-less, Shorthead, Chilian, Kaylaria, Sahara 3767, Sahara 3769, Erect Eared Barley, Himalaya, Orzo Nuda Putignans, Orzo Maraina, White Hull-less, Duckbill, Garton's Regenerated Maltster.
12. *Susceptible to P. anomala and P. graminis tritici 34, 45 and Resistant to P. graminis tritici 43.*
No. 78, Larissa.
13. *Susceptible to P. anomala and P. graminis tritici 43, 45 and Resistant to P. graminis tritici 34.*
No. 49, Primus, Meloy.

F1 TESTS OF RESISTANCE TO *P. GRAMINIS TRITICI*.

A number of crosses were made for these studies, based upon the reciprocal reactions shown to the four rusts. The F1 plants were tested and grown to maturity. It then became impossible to prosecute the studies, and later generation tests could not be made.

In the F1 tests of 37 crosses selected for their reciprocal resistance and susceptibility, there was dominance of resistance to race 43, and of susceptibility to races 34 and 45. No correlation with resistance to *P. anomala* was found. This also applied to three of the crosses in which resistance to *Erysiphe graminis hordei* was also involved.

RESISTANCE OF *ERYSIPHE GRAMINIS HORDEI*.

The occurrence of powdery mildew in the planthouse led to inoculation tests being carried out for resistance to *E. graminis hordei*. Later this was checked by recording the field behaviour in respect of the disease.

The following varieties were found to be resistant: C.I. 2269, C.I. 2215, C.I. 2237, C.I. 2280, C.I. 2218, C.I. 2250, Lion, No. 22, Psaknon, White Hull-less, Bolivia, C.I. 2329, Juliaca, Coast, Portuguese, Goldfoil, Hanna, Bark, Bolivia, Bel. 2071, Duplex, 017, Kwan, Weider.

SUMMARY.

Further studies are reported of resistance to leaf and stem rusts, and to a small extent to powdery mildew of barley.

Numerous F1 tests, with fewer back-cross, F2 and F3 studies, confirm the action, in the crosses studied, of a single dominant factor for resistance to *P. anomala*. This applies to varieties obtained from widely scattered sources.

Many F1 tests showed dominance of resistance to *P. graminis tritici* race 43, and of susceptibility to races 34 and 45 of this rust.

In the cases studied there was no evidence of correlation between leaf and stem rust or with certain morphological characters that were examined.

REFERENCE.

Waterhouse, W. L., 1927. *THIS JOURNAL*, 61, 218.

CORROSION OF SURFACES HEATED ABOVE THE BOILING POINT OF THE CORRODANT.

By R. C. L. BOSWORTH, D.Sc., F.A.C.I.

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The process of matter loss which occurs during the corrosion of metals appears to be controlled by many physical factors analogous to those which control the convective heat loss from geometrically similar hot bodies. When the temperature of a hot body immersed in a liquid is steadily raised beyond the boiling point of the liquid the curve of the emittance, and therefore the rate of boiling, plotted against the temperature takes a characteristic form. With rising temperature just beyond the boiling point there is first a steady rise in the emittance. At a certain temperature, however, a change occurs from film to nuclear boiling with an associated sudden drop in the emittance, which thereafter steadily rises with rising temperature. The work described in this note sets out to see if the rate of loss of matter by corrosion shows a similar behaviour when the temperature of the body subject to corrosion is slowly raised past the point at which nuclear boiling commences.

THE EXPERIMENTAL METHOD.

In the experimental measurement of corrosion from surfaces heated above the boiling point of the corrodant a hot wire device was used. The wire was heated by means of an electric current to a temperature which could be measured from the electrical resistance. Further, the rate of corrosion could be measured in terms of the rate of change of this resistance.

The wires examined were copper, the corrodants glacial acetic acid and acetic anhydride. A 5 cm. length of fine wire (38-46 gauge S.W.G.) was clamped on to current leads of the same metal. The clamps also held lighter voltage leads of the same metal. The specimen with its four leads was mounted in a cork stopper which fitted into a wide test tube containing the corrodant under examination. The test tube was mounted in a thermostatic bath maintained at the boiling point of the corrodant. The heating current was passed through a controlling resistance, an ammeter and the wire under test; and thus served to heat the wire above the boiling point of the corrodant and cause the liquid to boil on the wire. A voltmeter connected across the voltage leads enabled the resistance of the wire to be read. The quotient of the resistance obtained with the normal heating current over the resistance obtained with a very small current (of the order of 10 milliamps.) is a measure of the temperature (θ) above the boiling point of the liquid.

THEORY OF THE METHOD.

In an experimental run three measurements are taken—the time, the current I and the voltage drop V . The resistance R ($=V/I$) is related to the specific resistance (ρ) of the wire at the operating temperature T , and the radius (r) of the wire by

$$R=5\rho/\pi r^2 \dots\dots\dots (1)$$

5 being the length (in cms.) of the heated wire. For a change dr in the radius

of the wire a volume $2\pi r dr$ is lost from every unit length of the wire. The rate of corrosion q (in units of grams per sq. cm. per sec.) is then given by

$$q = \delta \frac{dr}{dt} \dots\dots\dots (2)$$

where δ is the density of the material of the wire. By substituting equation (2) in equation (1) we obtain

$$q = \delta \sqrt{\frac{5\rho}{\pi}} \frac{d(R^{-\frac{1}{2}})}{dt} \dots\dots\dots (3)$$

The quantity R , it should be recalled, is the resistance of a 5 cm. length of wire. From equation (3) we see that, provided the corrosion proceeds at a constant rate as the wire thins, the quantity $R^{-\frac{1}{2}}$ should vary linearly with the time.

The heat generated per unit surface area by the electric current is proportional to $I^2R^{3/2}$, and provided this factor is kept constant as the wire thins we may expect a constant surface temperature. (It seems reasonable to assume that the thermal transmittance will not vary as corrosion proceeds.)

EXPERIMENTAL RESULTS.

The samples examined were heated by various currents up to 20 amperes. On any fixed run the quantity $I^2R^{3/2}$ was kept constant, and $R^{-\frac{1}{2}}$ plotted against the time. Any given run was continued until either there was a ten per cent. change in the resistance or else the wire had fused. From the resistance measurements corrosion rates and temperatures were derived by the methods outlined above. The derived corrosion rates and temperatures (excess above the boiling point) are shown in the two figures. Figure 1 refers to copper in glacial acetic acid, and Figure 2 to copper in acetic anhydride.* It will be seen that the corrosion rates are quite large at the boiling points and rise steadily with further increase in the temperature, until, for temperatures of the order of 60° C. to 80° C. above the boiling point there is a sudden drop in the rate of corrosion, particularly in the case of acetic anhydride in which the rate of corrosion when the wire is 80° C. above the boiling point is only a small fraction of that when the wire is at the boiling point. Associated with this change in the rate is an equally obvious change in the chemistry of the reaction. At the lower temperatures copper dissolves to give a cupric salt which forms an intensely blue coloured complex with acetic anhydride. As soon as the temperature reaches the point at which the corrosion rate shows the sudden drop the blue colour begins to disappear and in its place there appears first a yellowish muddy fluid and finally a flocculent pink precipitate, apparently cuprous oxide or a basic cuprous acetate. Once the pink precipitate has formed no further corrosion apparently takes place and the supernatant liquid remains colourless. This is particularly remarkable in that the leads, which are not protected by a vapour film and have a surface area exposed to the liquid much larger than that of the hot wire, also appear to cease dissolving in the corrodant when attack on the hot wire ceases.

DISCUSSION.

There are two points of interest in this work. In the first place it appears that a copper heating surface in acetic anhydride may be protected from corrosion if the temperature of the copper is high enough. One might compare this phenomenon with the drop in heat transfer coefficient which occurs when the temperature of a heating surface is made sufficiently high (see for example

* The corrosion rate in these two figures is measured in the customary units of mgrms. dec.⁻² day⁻¹.

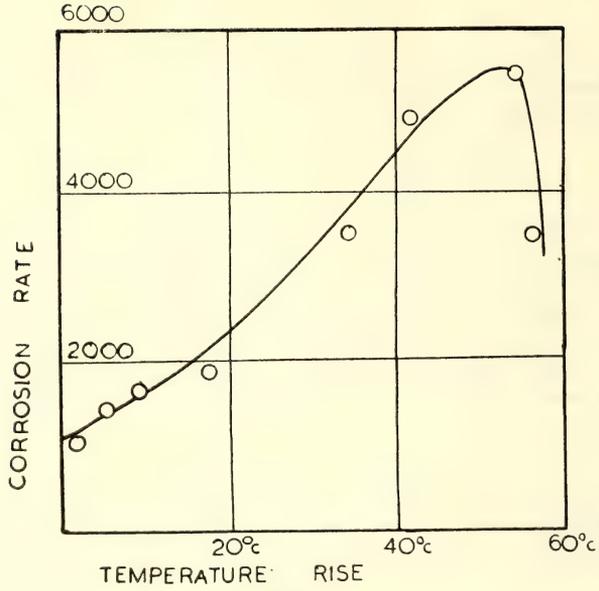


Fig. 1.

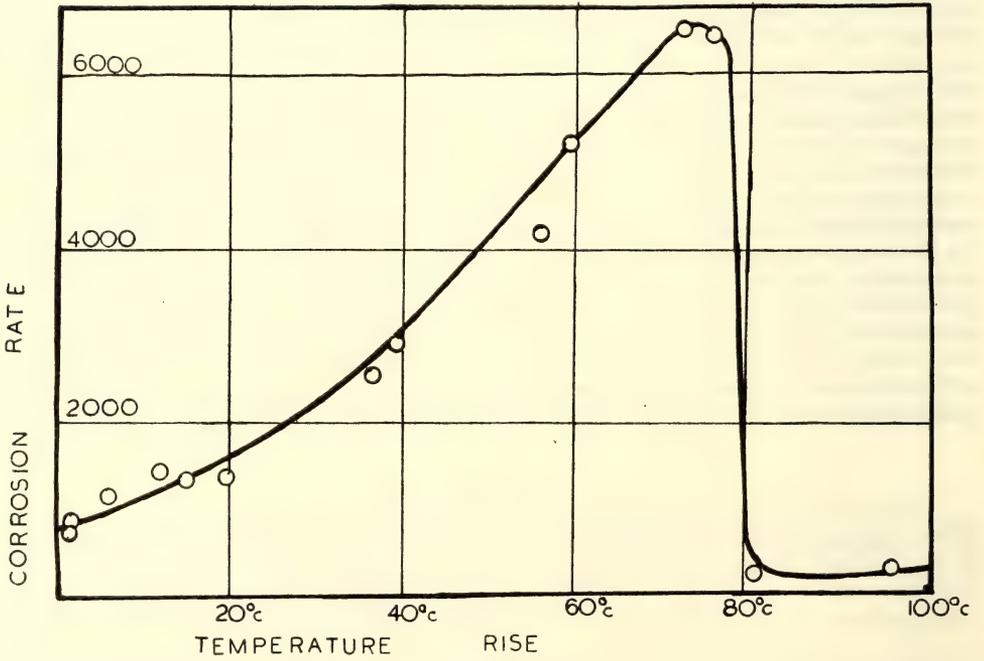
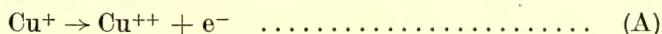


Fig. 2.

Bosworth, 1946). Presumably the same cause is responsible for both phenomena, namely the formation of a complete vapour film over the surface.

In the second place these experiments give an interesting indication of the part played by the equilibrium between the cuprous and the cupric ions in the corrosion of copper. This subject has been treated by Gatty and Spooner (1938). In the oxidative reaction



dissolved oxygen acts as the electron acceptor. The reverse reaction will only proceed at an appreciable rate heterogeneously at an interface. When this occurs at a copper-electrolyte interface a corrosive reaction is involved, namely



It now appears that when the copper surface is covered with a vapour film, the reverse of equation (A) occurs at the vapour liquid interface leading to the reduction of cupric to the cuprous state without progressive attack on the copper surface.

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 Gatty, O., and Spooner, E. C. R. (1938). *The Electrode Behaviour of Corroding Metals in Aqueous Solutions*. Oxford, pp. 182-252.



A NEW METHOD FOR THE COMPARISON OF THE THERMAL CONDUCTIVITIES OF FLUIDS.

PART II.

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SCOPE OF THE INVESTIGATION.

In Part I of the series of papers on this subject (Bosworth, 1947) it was shown that the relative thermal conductivities and convective moduli of fluids could readily be obtained from a series of measurements of the rate of heat loss (q) and the excess temperature (θ) when a hot wire is immersed successively in the fluids to be compared. The quantity q/θ is plotted against $\theta^{1/3}$. The points for any one fluid and given hot wire when thus plotted were shown to fall on a straight line. With a given wire the intercepts on the q/θ axis were shown to be proportional to the thermal conductivities (k) of the fluids under test, while the slopes were shown to be proportional to $ka^{1/3}$, where a , the convective modulus, is related to other physical properties of the fluid by

$$a = \frac{\rho^2 c g \beta}{\eta k} \dots\dots\dots (1)$$

with ρ the density,
 c the heat capacity at constant pressure,
 β the coefficient of volumetric expansion,
 η the viscosity, and
 g the acceleration due to gravity.

The heat loss factor for a resistance wire heated by an electric current (I) is directly proportional to I^2 , while θ the excess temperature may readily be measured by using a thermocouple with one junction on the surface of the wire and one immersed in the fluid.

Instruments of this type were used in comparing the thermal conductivities and convective moduli of a number of common fluids with the corresponding properties of water. Except for the more volatile fluids the relative figures obtained by this method were found to be in satisfactory agreement with the best figures from the literature. Since the method is essentially a comparative one, it was suggested that it would be of outstanding value in the measurement of the thermal conductivities of binary mixtures.

The present paper takes up the subject with the study of the thermal conductivity and convective moduli of aqueous solutions of potassium chloride, sucrose and glycerine at 27° C., and obtains, for each of the systems, the properties above as a function of the concentration.

An empirical equation connecting the thermal conductivity (k) of a binary mixture of fluids with the thermal conductivities (k_1) and (k_2) of the components has been given by Barratt and Nettleton (1929). Their equation reads :

$$k \text{ Sinh } 100\mu = k_1 \text{ Sinh } p \mu + k_2 \text{ Sinh}(100 - p)\mu \dots\dots\dots (2)$$

where p is the weight percentage of the first component and μ is a factor which varies with the constituents and the temperature. A table of the values of μ

given by Barratt and Nettleton has been amended by Bates, Hazzard and Palmer (1938), who also found equation (2) to give satisfactory accounts of the thermal conductivity of liquid mixtures. In assessing the value of the method of measurement under examination we thus have three independent modes of comparison; published data for the thermal conductivities of the mixture, empirical equation (2) and the fact that the various properties entering into the determination of the convective modulus are, with the exception of the thermal conductivity, comparatively well known, so that it is possible to check the method for self consistency by independent measurements of the thermal conductivity and the convective modulus.

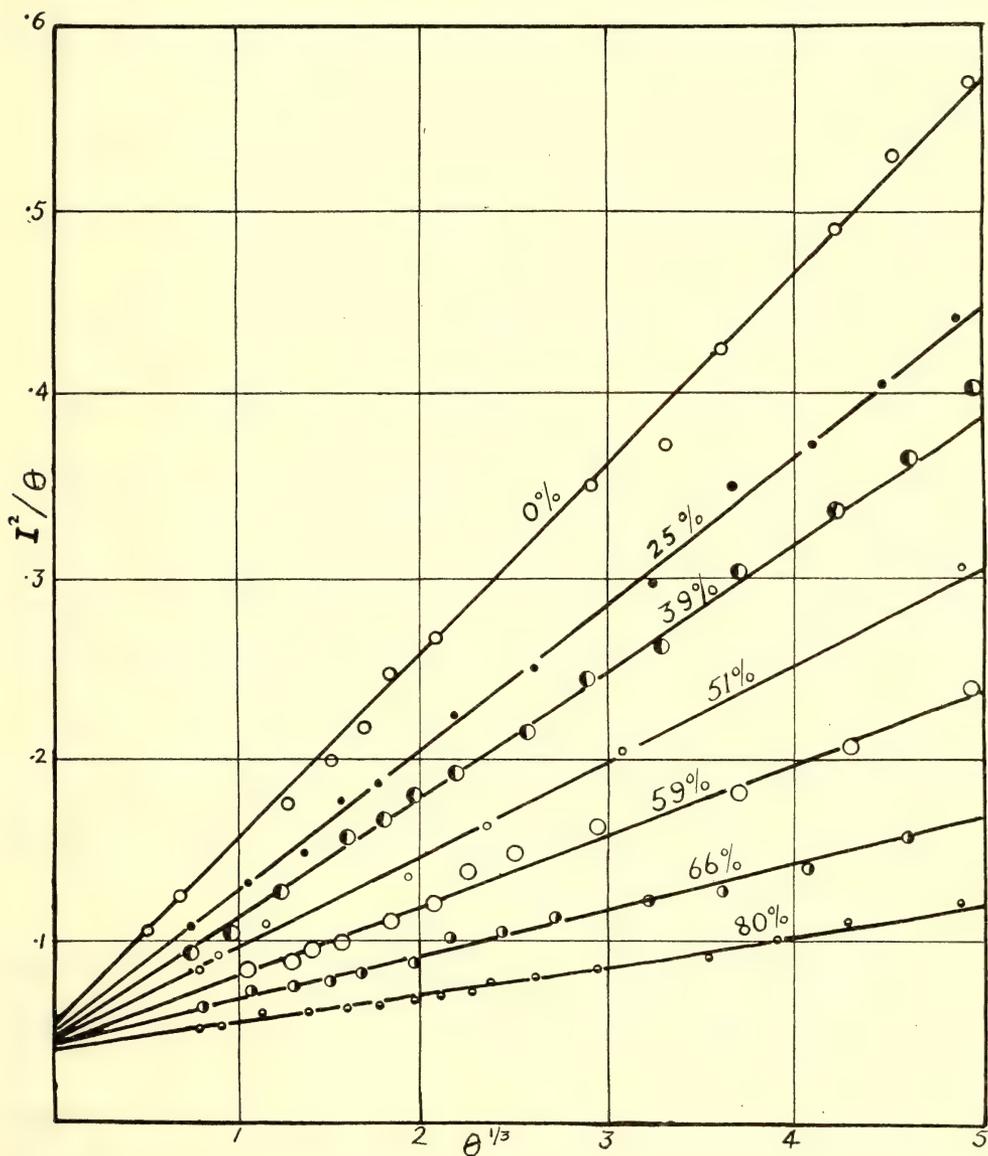


Fig. 1.

EXPERIMENTAL RESULTS.

The experimental arrangements and procedure were the same as that described in the earlier paper (Bosworth, 1947). Results were first obtained as a series of readings of I versus θ . Data for any particular system were then plotted in the form of I^2/θ versus $\theta^{1/3}$. Figure 1, for example, shows the data obtained from a series of sucrose solutions plotted in this way. The top (and steepest) curve refers to the results from pure water and the others in order refer to 25%,

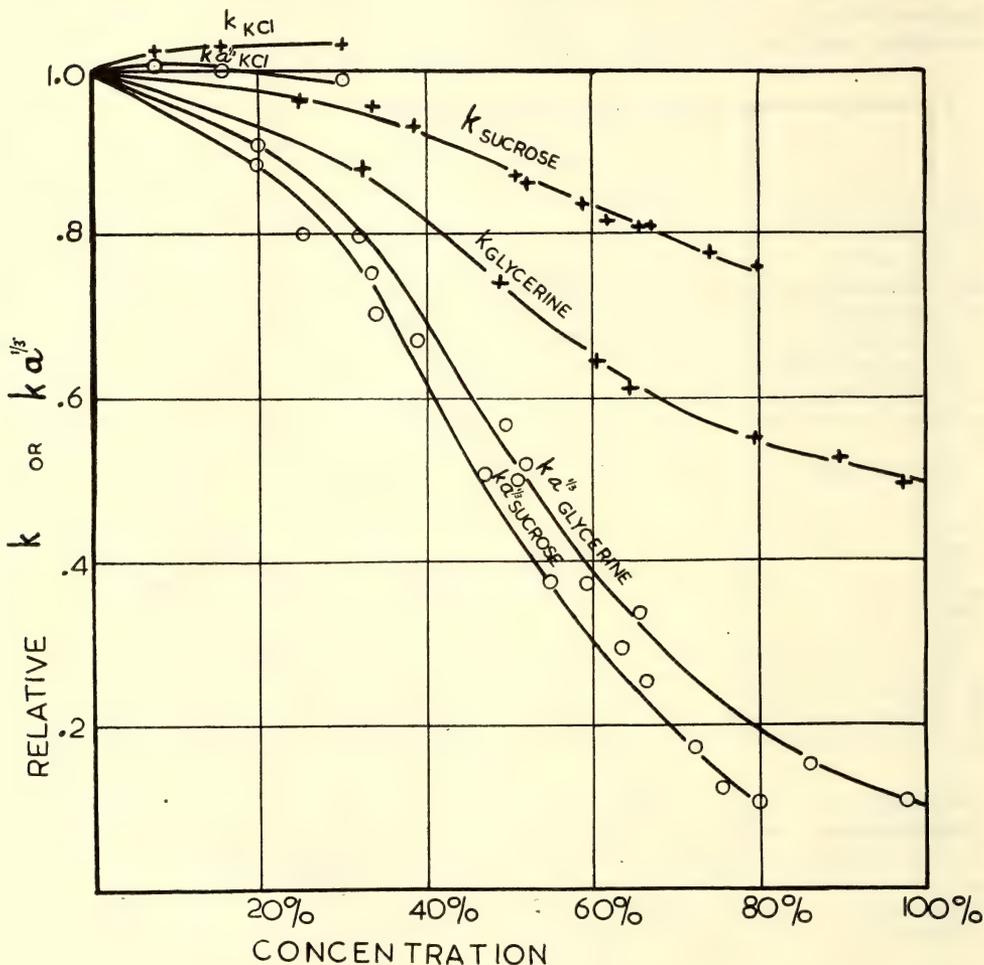


Fig. 2.

39%, 51%, 59%, 66% and 80% sucrose solutions, all at 27° C. and all expressed as weight per cent. of sucrose on the weight of the solution. The lowest curve (80%) refers to a metastable (supersaturated) solution. No detectable crystallization took place during the determinations, but the solution crystallized on standing afterwards.

A similar series of curves were obtained for solutions of potassium chloride in water and for mixtures of water and glycerine. The completed data from these three sets of determinations are shown in Figure 2, where curves are given for the variation of the intercepts and slopes plotted against the weight per-

centage composition of the fluid for all three systems. The points marked with crosses refer to the intercepts (or relative thermal conductivities) and those with circles to the slopes (proportional to $ka^{1/3}$). In the KCl system it will be seen that the addition of the salt increased the thermal conductivity by about 3%, while the addition of the other two substances lowered the thermal conductivity. The slopes were all decreased with increasing concentration of the solute except in the case of the more dilute KCl solutions where the slope is slightly greater than unity for ranges of concentration up to 15% KCl.

DISCUSSION OF THE SYSTEM KCl-WATER.

Figures for the relative thermal conductivities and convective moduli at various concentrations have been calculated from the data given in Figure 2. The results are tabulated in Table I.

TABLE I.

Relative Thermal Conductivities and Convective Moduli for KCl Solutions.

Concentration Wt. %.	Relative Thermal Conductivity.	Relative Convective Moduli.
0.0	1.000	1.000
5	1.020	0.96
10	1.025	0.94
20	1.030	0.90
30	1.030	0.85

The slight rise in the thermal conductivity produced by the addition of KCl to water has been recorded before (*International Critical Tables*, Vol. V (1928)). The fall in the convective modulus with increase in concentration is, primarily, a consequence of the increase in viscosity with increasing concentration. Thus the viscosity of a 30% solution of KCl at 25° C. is given in the *International Critical Tables* as some 15% higher than that of pure water, while the table above shows that the convective modulus is 15% lower.

DISCUSSION OF THE SYSTEM SUCROSE-WATER.

Values of the relative thermal conductivity and convection modulus of sucrose solutions are given in Table II as a function of the concentration. There

TABLE II.

Relative Thermal Conductivities and Convective Moduli of Sucrose Solutions at 27° C.

Concentration Wt. %.	Relative Thermal Conductivity.	Relative Convective Modulus from	
		Measurement.	Calculation.
0	1.00	1.00	1.00
20	0.98	0.70	0.57
40	0.93	0.31	0.27
50	0.88	0.17	0.17
60	0.83	0.070	0.056
80	0.76	0.0020	0.0021

are four columns in this table. The first gives the concentration, expressed as a weight per cent., the second the relative thermal conductivity calculated from Figure 2, the third the relative convective modulus calculated from the same source, and the fourth the relative convective moduli calculated from the thermal conductivities given in column 2 combined with the other physical properties: densities, specific heats, coefficients of thermal expansion and viscosities. The figures for the viscosities were taken from the International Critical Tables and, for the more concentrated solutions from Lyle (1941); the specific heats were calculated from the formula of Yanovsky and Archangelsky (1928) and the densities and the coefficients of thermal expansion were calculated from the tables of Spencer and Meade (1945).

The excellent agreement between the figures in columns 3 and 4 may be taken as confirming the accuracy of the experimental figures given in column 2. However, the thermal conductivity versus composition curve cannot be made to follow any expression of the type of equation (2). The change in thermal conductivity produced by the addition of a small amount of extra sucrose to a dilute solution is less than that produced by the addition of the same quantity to a concentrated solution.

DISCUSSION OF THE SYSTEM GLYCERINE-WATER.

This system has been studied from 100% water to 100% glycerine. All the relevant data at 27°C. may be obtained from Figure 2. A summary of these results is given in Table III, which includes columns of measured and of calculated figures.

TABLE III.

Relative Thermal Conductivities and Convective Moduli of the Binary System Glycerine-Water at 27°C.

Concentration Wt. % Glycerine.	Relative Thermal Conductivity from		Relative Convective Modulus from	
	Measurement.	Calculation.	Measurement.	Calculation.
0	1.00	1.00	1.00	1.00
20	0.94	0.87	0.79	0.79
40	0.82	0.75	0.57	0.60
50	0.73	0.69	0.42	0.49
60	0.64	0.65	0.26	0.30
80	0.55	0.56	0.064	0.076
100	0.48	0.48	0.0076	0.0052

The figures in column 2 are the relative intercepts from Figure 2. The figures in column 3 were calculated from a formula of the Barratt and Nettleton type using the revised values of the constants given by Bates, Hazzard and Palmer (1938). It will be seen that while the agreement is excellent at the higher concentrations, it is not so at the lower concentrations. Once again these results have indicated a relatively smaller change of thermal conductivity with concentration change in the more dilute solutions. The calculated convective moduli, given in column 5 above, were obtained from thermal conductivities from column 2, data for density and coefficient of thermal expansion from Bosart and Snoddy (1928), data for viscosity from Shelly (1932), and for the specific heats from the International Critical Tables. The agreement with the measured

convective moduli is excellent and the suggestion made originally that this particular method of measurement should be very suitable for binary mixtures appears to be amply justified.

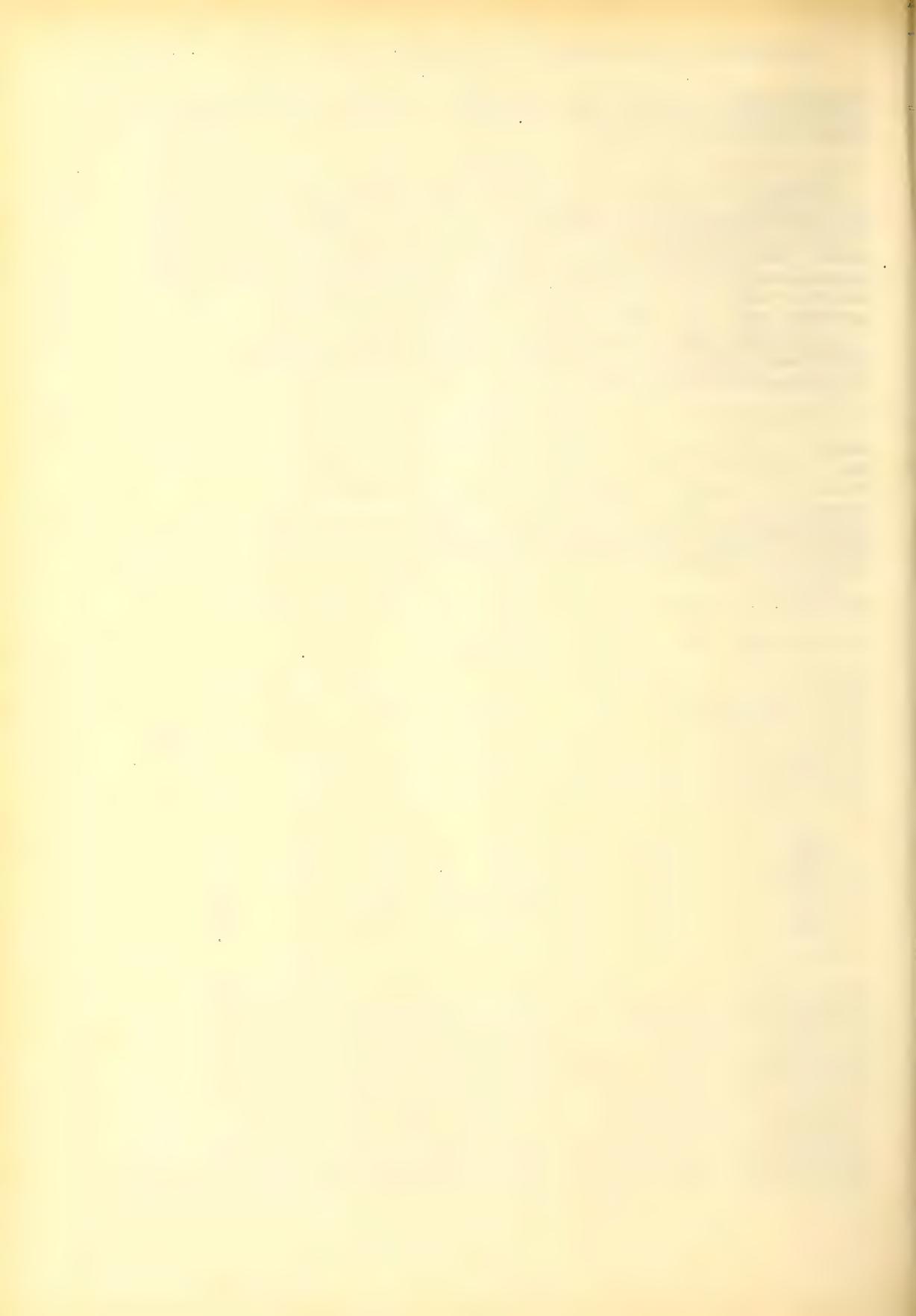
SUMMARY.

The thermal conductivities and convective moduli of binary solutions of KCl-water, sucrose-water and glycerine-water at 27° C. have been measured as a function of the concentration by the method described in the first paper of this series. The results are shown to be self consistent in that values of the convective modulus calculated from the measured thermal conductivity and the generally accepted values of other physical properties of the solutions are in excellent agreement with those obtained by direct measurement.

In the case both of sucrose-water and of glycerine-water the addition of further solute produces a relatively larger change in the thermal conductivity of the more concentrated solutions.

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OF
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and Index**

EDITED BY
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Honorary Editorial Secretary

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PART IV

THE CHEMISTRY OF BIVALENT AND TRIVALENT IRIIDIUM.

PART IV. THE OXIDATION-REDUCTION POTENTIAL OF THE BROMIRIDATE-BROMIRIDITE SYSTEM.

By F. P. DWYER, D.Sc.,
H. A. MCKENZIE, M.Sc.,
and R. S. NYHOLM, M.Sc.

Manuscript received, October 9, 1947. Read, November 5, 1947.

In a previous communication (Dwyer, McKenzie and Nyholm, 1944) it was shown that the chloriridate-chloriridite system behaved as a typical anionic system, the potential rising with increasing ionic strength. The bromiridate-bromiridite system was similarly expected to be anionic, with the potential at a somewhat lower value owing to the greater stability constant of the bromiridate ion. This was found to be the case, but the chief interest in the system was in a unique phenomenon of reduction of the oxidant at moderate and high ionic strengths.

When solutions of potassium hexabromiridate and hexabromiridite were mixed in hydrobromic acid solution the deep violet colour of the oxidant ion was found to lighten appreciably especially when the acid concentration was high. At the same time the odour of bromine could be detected. Pure potassium bromide and also potassium nitrate in the presence of a little hydrobromic acid also led to lightening of the colour and if sufficient potassium bromide or potassium nitrate were added to the solution almost complete decolorization resulted.

The phenomenon appears to be dependent on the opposite effects of ionic strength on the bromiridate-bromiridite and bromine-bromide systems. The potential of the bromine-bromide electrode (E° , 1.08 volts) falls with increasing ionic strength, while that of the bromiridate-bromiridite system (E° , 0.99 volt) rises with increasing ionic strength. The potentials of the two systems thus approach each other as the ionic strength is increased and finally bromide ion is oxidized to bromine, whilst the violet bromiridate ion is reduced to the pale yellow bromiridite ion.

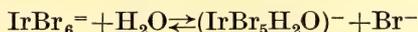
From equilibrium considerations if E'_0 and E''_0 are the respective redox potentials of the bromine-bromide and bromiridate-bromiridite systems, then

$$E'_0 - E''_0 = 0.06 \log \frac{(\text{Br}^-)(\text{IrBr}_6^-)}{(\text{Br}_2)^{\frac{1}{2}}(\text{IrBr}_6^{\equiv})}$$

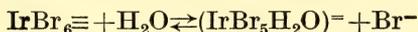
If the ratio of bromiridate and bromiridite ions is kept constant, the reduction of the former will be determined by the potentials of the two systems at the particular ionic strength and by the concentration of bromide ions. If insufficient bromide ion is present, reduction of the bromiridate cannot take place. The concentration of bromide ion arising by dissociation of the bromiridate ion is not sufficient, and solutions of bromiridate in excess of potassium nitrate are quite stable towards reduction.

Freshly prepared dilute solutions of potassium or ammonium hexabromiridate in very dilute hydrobromic acid were violet and gradually changed to indigo blue, but the violet colour could be regenerated by the addition of hydrobromic

acid and a little bromine. This effect could not be produced with other acids and suggests that an aquo compound is formed



Similarly potassium bromiridite prepared by reduction with alcohol in the presence of much hydrobromic acid formed a brownish yellow solution which was oxidized by bromine to the violet bromiridate, but if the solution in dilute hydrobromic acid was allowed to stand it gave the blue compound on oxidation. It thus appears that an equilibrium also exists with the reductant ion



In very weakly acid solutions the potential changes produced by the addition of nitric acid indicated that true hydrolysis (formation of hydroxy complexes) could also occur. Although not mentioned in the original paper, equilibria of this sort undoubtedly exist in solutions of chloriridates and chloriridites. Potassium aque pentachloroiridite has been described by Delepine (1908) and this substance on oxidation gives a dark brown solution of (probably) potassium aquo pentachloroiridate. This latter substance has not yet been described. The potentials quoted for both systems are thus more correctly the potentials of the equilibrium mixtures rather than the simple systems.

EXPERIMENTAL.

Potassium Hexabromiridate.

Black octahedra of this substance were prepared by Gutbier and Priess (1909) by boiling the chloro compound with potassium bromide. The present authors were unable to obtain the substance by this method but found that if the chloro compound were boiled for some hours with hydrobromic acid reduction gradually occurred and the bromo compound could be obtained by oxidizing with bromine in the presence of potassium bromide.

However, in order to avoid contamination with unchanged chloro compound, the substance was finally prepared by refluxing purified potassium hexanitroiridite with concentrated hydrobromic acid and bromine. During the reaction an undescribed nitroso compound appeared to be formed as a reddish crystalline precipitate, especially in the absence of bromine, but finally the solution became deep violet and on cooling deposited black octahedra of the required substance. The identity of this material was checked by X-ray powder photographs, which showed it to be face centred cubic, isomorphous with ammonium chloroplatinate. The substance was finally recrystallized several times in the presence of bromine and a little hydrobromic acid. The solution used in the potential studies was 0.01 M with respect to iridium and 0.028 M with respect to hydrobromic acid.

Potassium Hexabromiridite.

Half of the bromiridate solution was treated with hydrobromic acid and alcohol and evaporated over a water bath, adding more alcohol from time to time. The correct amount of potassium bromide was then added, followed by hydrobromic acid and alcohol. After evaporation to dryness a greenish brown residue was left, which dissolved in dilute hydrobromic acid to a pale brownish yellow solution. This was analysed for iridium and finally adjusted to 0.01 M with respect to iridium and 0.0052 M with respect to hydrobromic acid.

MEASUREMENT OF THE REDOX POTENTIAL.

The apparatus, electrodes and general procedure were similar to those used for the chloriridate-chloriridite system. The temperature of measurement was 20° C. In view of the sensitivity of the system to reduction, the bromiridate was always added last when preparing the various solutions. However, owing to the complex equilibria involved, their slowness of establishment, and the tendency of the solutions to lose bromine, reproducible potentials were difficult to obtain

from different batches of bromiridate and bromiridite. The potentials are thus considered not more accurate than ± 5 mv. The uncertainty in the absolute value of the potentials does not affect the shape of the curves or the general conclusions. Care was taken to obtain the whole of the curves shown with the same batch of oxidant and reductant.

RESULTS.

In the first series of determinations the iridium concentration was kept constant and the concentration of hydrobromic acid varied. The potential rose and then fell away sharply owing to reduction of the oxidant and loss of bromine from the solution (Table I and curve 1).

TABLE I.
Iridium Concentration Constant ($I=0.0030$) and Hydrobromic Acid Concentration Varied.

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0033	0.05	0.961
0.0050	0.071	0.989
0.0070	0.084	0.994
0.0100	0.100	0.996
0.0233	0.153	0.991
0.1523	0.390	0.962

In the second series a small constant concentration of bromide and iridium was maintained and the ionic strength raised by the addition of nitric acid (Table IIA and curve 2). The potential rose with increasing ionic strength, but the pronounced falling away at high ionic strengths did not occur. The steep slope at low acidities can be attributed to true hydrolysis. This curve is similar in shape to that obtained for the chloriridate system in hydrochloric acid solution. If extrapolated from the point where hydrolysis becomes serious to infinite dilution, assuming the validity of the Debye Huckel limiting law, an approximate value of 0.990 ± 0.005 volt for the redox potential at infinite dilution is obtained.

TABLE IIA.
Iridium Concentration Constant ($I=0.0060$), Bromide Ion Concentration Constant ($I=0.0006$), Nitric Acid Concentration Varied.

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0065	0.081	0.970
0.0082	0.091	0.988
0.0098	0.099	0.998
0.0149	0.122	1.007
0.0182	0.135	1.008
0.0232	0.153	1.010
0.0398	0.199	1.014
0.167	0.408	1.030

Table IIB shows the effect of nitric acid on the potential for the same iridium concentration but a greater concentration of bromide ions. It will be noticed that the bromide ion concentration is still insufficient to permit reduction.

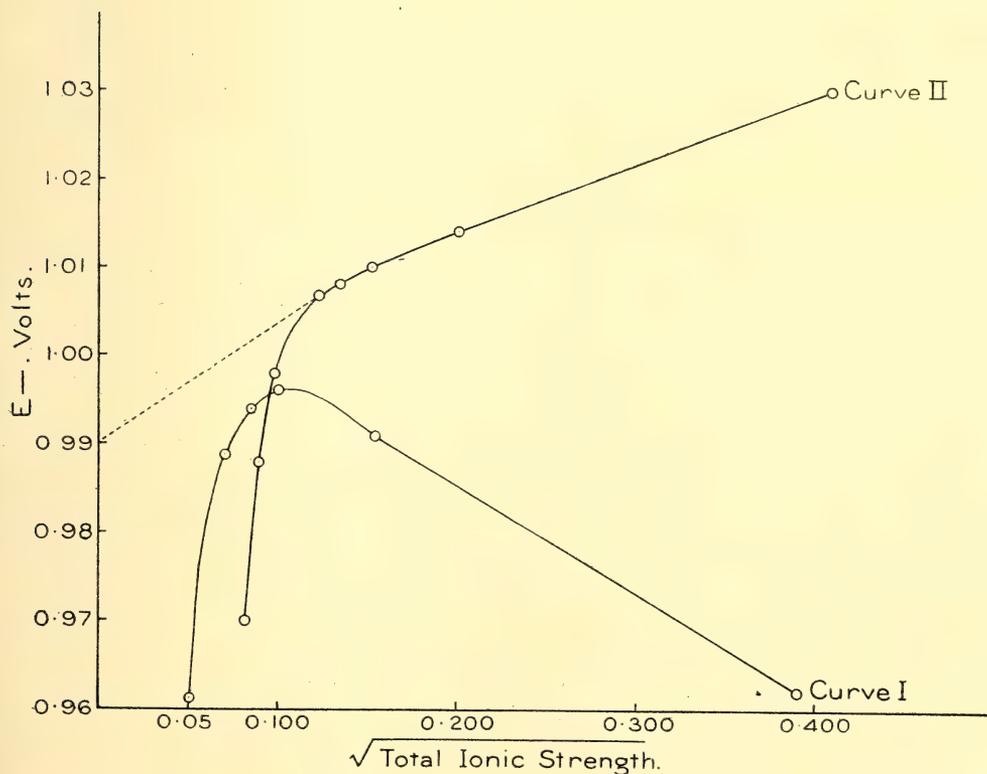
In the third series (Table III) the iridium concentration was maintained at the same value, nitric acid was added in sufficient constant amount to prevent

TABLE IIB.

Iridium Concentration Constant ($I=0.0060$), Bromide Ion Concentration Constant ($I=0.0023$), Nitric Acid Concentration Varied.

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0083	0.0906	0.983
0.0115	0.107	0.999
0.0150	0.122	1.002
0.0183	0.135	1.012
0.0248	0.153	1.010
0.0285	0.168	1.012
0.0332	0.182	1.013
0.0415	0.203	1.014

Curves I, II



hydrolysis, and the ionic strength raised with potassium bromide. The potential fell away sharply owing to reduction of the bromiridate and loss of bromine.

TABLE III.

Iridium Concentration Constant ($I=0.0060$), Bromide Ion Concentration Varied, Nitric Acid Concentration Constant ($I=0.0100$).

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0165	0.129	1.008
0.0265	0.163	1.004
0.0332	0.183	0.993

SUMMARY.

The oxidation reduction potential of the bromiridate-bromiridite system at infinite dilution was found to be 0.99 volt at 20° C. The system behaved as a typical anionic system, but a unique feature was the reduction of the oxidant by bromide ion as the ionic strength was raised.

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THE GEOLOGY OF THE STANHOPE DISTRICT, N.S.W.

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With Plate V and three text-figures.

Manuscript received, October 16, 1947. Read, November 5, 1947.

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INTRODUCTION.

The Stanhope District is situated on the northern side of the Hunter River about eight miles north of Branxton and about 140 miles from Sydney.

The area studied is of approximately 50 square miles, bounded to the east by Lamb's Valley Road, to the west by the Hunter overthrust fault, to the south by the Hunter River, and to the north by the Webber's Creek fault.

Walkom (1913) published a paper on the geology of the Glendon Brook District in which the geology of the Cranky Corner Basin and a general survey of the geology surrounding the basin is given. However, Osborne (1926) examined in detail and published the geology of a portion of this area, the Mirannie and Mt. Dyrning District, which lay to the north-west of the Stanhope District and is bounded by the Webber's Creek fault. The general geology of the Gosforth District which links up with that of the Stanhope District along Lamb's Valley Road to as far north as the bridge across Lamb's Creek was published by Browne (1926). Osborne (1927) published the geology of the area between Paterson and Lamb's Valley which links up with that of the Stanhope and Gosforth Districts to the north.

The Stanhope District affords the geologist with representatives of both the Volcanic and Glacial Stages of the Kuttung as well as most stages of the Permian, which, with the exception of those of the Cranky Corner Basin, have been faulted against the Kuttung rocks. The district also yields its share of the great structural pattern of the Hunter River District.

PHYSIOGRAPHY.

The Stanhope District is only a small area in a larger physiographic unit, the Hunter River District. The topography of the Hunter River District has an aspect of late maturity and is the result of stream action upon a peneplain which was elevated, with a tilt to the south, to a plateau during the Kosciusko uplift at the close of Tertiary time. Browne (1926) regards the peneplain before uplift as probably being continuous with the Hawkesbury sandstone country of the Broken Back Range and other high land to the south and south-west. In all probability the Hunter River District matured at an early stage as a result of the unresistant nature of the soft Permian strata and old fault planes in the Kuttung strata through which the river flows.

Viewing the physiography of the Stanhope District from the rise on the southern bank of the Hunter River at a point midway between Lamb's Valley Road and Elderslie, the most noteworthy feature is the relationship of topography to the geological structure. To the north about $2\frac{1}{2}$ miles from the river there suddenly rises the southern edge of a dissected plateau, which extends from Lamb's Valley Road in the east, where it almost takes a right-angled bend to the north having been dissected by Lamb's Creek, and to Elderslie in the west, where it also takes a bend almost at right angles to the north. A few remnants, such as Tangorin, 1,554 feet, Durham Peak, 1,250 feet and Lamb's Mountain, 1,100 feet, form eminences on the plateau and indicate its height. This plateau is an excellent example of the relationship of the geology to the physiography. Its edge is a dip escarpment of toscanite, which in comparison with the softer underlying tuffs and tuffaceous conglomerates is more resistant to erosion. To the east the volcanic rocks, such as toscanite, pyroxene andesite and rhyolite, give rise to a series of hills, which appear as a succession of dip slopes and dip escarpments and trend in an east-west direction, while to the west the area examined is bounded by two rows of hills trending in a north-south direction, the one further west being the higher composed of conglomerate and felsite, the other composed of hornblende andesite.

In the foreground from the point of observation is gently undulating country, 50-300 feet high, bound on all sides by the higher land described above. This country for the most part consists of conglomerates, tuffs and thin bands of volcanic lavas. It has been dissected by small creeks.

The faulting, which has occurred in the area, has not given rise to fault scarps. This is probably due to the fact that faulting antedated the uplift of the peneplain. On the other hand the faults have played a considerable part in the determination of the physiography, for in most cases the faulting has resulted in the softer Permian rocks having been brought up against the harder Kuttung lavas. This is evident in the western portion of the district, where the Hunter overthrust fault has brought the Permian sediments up against the Kuttung conglomerates and lavas, the result being that the more resistant Kuttung rocks give rise to the row of hills trending north-south. East of this fault one sees the more or less rugged physiography of the Carboniferous rocks, while to the west of it the physiography is gently undulating.

The most important feature of the Hunter River physiography is the river itself. The part of it which flows through the area under examination is characterised by much meandering, indicating a very mature stream. Its course in some parts can be explained by the geological formations. For instance, in the Stanhope District, the river flows in an easterly direction, its course being determined by the Hunter overthrust fault. The flood plains on the northern side of the river are rather narrow but nevertheless it has built wider flood plains on the concave sides of the meanders and practically none on the convex sides.

Two levels of alluvium are present along the northern bank of the river. These river terraces are at heights of 100' and of 50' above the present day river

bed. They indicate subsequent minor uplifts, which have enabled the river to cut down through its former flood plains to a new base level. In parts, for example near Goodyear's, the river has completely eroded away the lower of the two terraces and has revealed good rock sections.

Three important tributaries of the Hunter River are Glendon Brook, Stanhope and Lamb's Creeks, all of which have a mature aspect in parts, being characterised by much meandering. Glendon Brook appears to have taken advantage of the Hunter overthrust and Webber's Creek faults. The valley of Lamb's Creek is impressive physiographically. It is a wide U-shaped valley, the particular shape being due to the hard thick capping of toscanite underlain by softer tuffs and conglomerate. To account for the wide valley the creek seems to represent a shrunken remnant of a very impressive stream, which probably existed in earlier times. Today all one sees is a narrow creek meandering along the middle of the wide valley floor.

Stanhope Creek, whilst revealing evidences of maturity in parts, has not carved out such an impressive valley. It has carved a rather narrow V-shaped valley through the toscanite before it enters the undulating country between the plateau and the Hunter River. Both the Stanhope and Lamb's Creeks show evidence of youth towards their sources in the plateau area. In this region intermittent waterfalls occur along their courses due to resistant bands of rock such as the toscanite.

All of the hills are characterised by talus slopes and it is through these slopes that numerous small consequent streams are cutting their beds. Along the edge of the Tangorin Range to the north and east and the Moonabung Plateau to the east of Lamb's Valley Road these streams are seen to occur at intervals of about 50 yards. In most cases these creeks are cutting across the strike of the beds and link up with one of the more important creeks. For example those from the Moonabung Plateau link up with Lamb's Creek in the east and with Stanhope and Dutton's Creeks in the south and Glendon Brook in the north. Quite often the creeks have taken advantage of minor faults and joint planes. Dutton's Creek is an example of this. Just before it joins the Hunter River it has taken advantage of the weakness along the Hunter overthrust fault. The creek running beside the Cranky Corner Road has carved out a deep valley through hard rhyolite, conglomerate and toscanite.

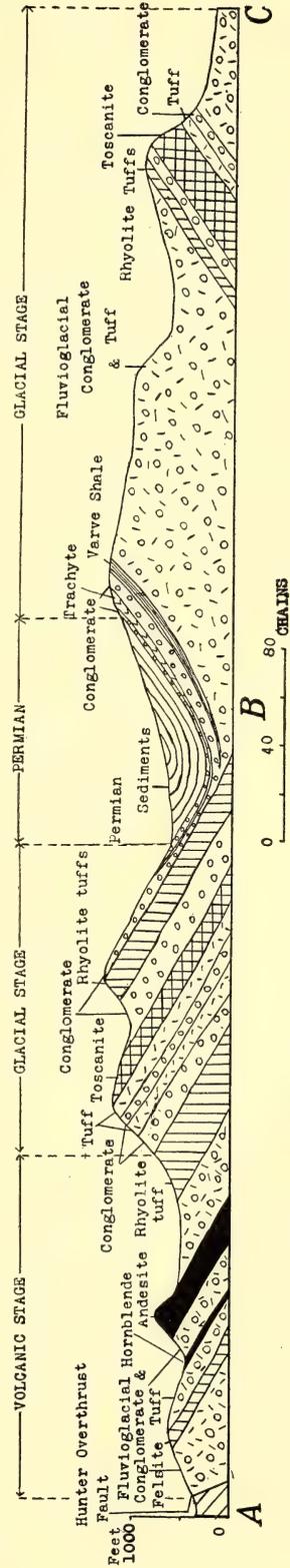


Fig. 1.—General Geological Section across Stanhope Area. (Line A-B-C on map).

Evidences of numerous slickensides in the rocks along Cranky Corner Road indicate instability even though there is no evidence of a fault.

STRATIGRAPHY.

Carboniferous.

The Carboniferous rocks in New South Wales may be divided into two main divisions, namely the Burindi which consists of the marine beds, and the Kuttung which consists of terrestrial beds, these being glacial and volcanic for the most part. In the Stanhope District rocks of the Burindi Division are entirely absent but both glacial and volcanic beds of the Kuttung are well represented.

Osborne (1922) has divided the Kuttung rocks into (a) Basal Stage, (b) Volcanic Stage, and (c) Glacial Stage. In the district studied no example of the Basal Stage type has been found, but it appears as though the Volcanic Stage is equivalent to the combined Basal and Volcanic Stages of Osborne. See Figures 1 and 2.

Volcanic Stage. In the Stanhope District rocks of the Volcanic Stage are very well developed. All the series determined by Browne in the adjacent Gosforth District have been recognised. The volcanic series extends westwards for about seven miles in an unbroken arc from Lamb's Valley in the east to Elderslie in the west, where they swing to the north to Glendonbrook. At Elderslie they are cut along the strike by the Hunter overthrust fault, which extends northwards and across the strike at Glendonbrook by the Webber's Creek fault.

The series consists of the following flows :

	Feet.
Dacite tuffs and ignimbrites (including dacitic pitchstone)	800
Toscanite	260
Toscanite	400
Hornblende andesite (and hornblende andesitic pitchstone)	900
Pyroxene andesite (and pyroxene andesitic pitchstone)	1,200
Hornblende andesite (and hornblende andesitic pitchstone)	130
Felsite	160
Felsite	130
Pyroxene andesite	50
Pyroxene andesitic pitchstone	—
Rhyolite	920
Pyroxene andesite (and pyroxene andesitic pitchstone)	660
Rhyolite (faulted along strike)	—
Total	5,610

Each of these flows is separated over the greater part of the area by varying thicknesses of fluvio-glacial conglomerate and interbedded tuff. An average section through the Volcanic Stage is approximately 5,400 feet in thickness.

The lowest flow of the Volcanic Stage represented in the Stanhope District is seen outcropping along the northern bank of the Hunter River at the base of John's Hill and near Miss Bendeich's house. It is a very light coloured felsitic type of rock consisting of tiny phenocrysts of quartz and biotite. Its thickness cannot be ascertained as the flow has been dislocated along its outcrop by the Hunter overthrust fault which has also caused the rhyolite to be turned up steeply.

Immediately overlying this rhyolite is the lower flow of pyroxene andesite which resembles that of the upper flow described below. It is underlain by a thin flow of pitchstone.

The next flow is more or less the lowest rhyolite flow of importance. This rhyolite is very persistent and outcrops from Lamb's Valley Road along both sides of the Stanhope Road, crosses the road in front of H. Bendeich's property and continues east-west until it is cut out by the Hunter overthrust fault near Dutton's Creek. John's Hill between Stanhope Road and the Hunter River is composed of this rhyolite, which has given rise to a dip slope to the north and a dip scarp to the south. The rhyolite varies in character throughout the flow. At Lamb's Valley the rock is pinkish brown in colour, exhibiting excellent flow structure on a relatively large scale and containing veins of chalcedony. In places where the flow structure is not so predominant the phenocrysts are more distinct and appear to be lath-shaped crystals of orthoclase. The rock contains fragmentary inclusions. Behind W. Bendeich's house the rock is a brownish andesitic type containing small phenocrysts of plagioclase. There is also underlying this phase in the same area a light pink coloured rock which seems to resemble a weathered phase of the Lamb's Valley type. At the back of Harrigan's the next phase occurs. This consists of phenocrysts of orthoclase and abundant glassy quartz in a dark brown coloured stony groundmass. West of John's Hill the rhyolite is separated by a thin band of tuff and conglomerate. The felsite above the sedimentary rocks is lighter coloured, having a bluish grey matrix, fawn when weathered, with larger phenocrysts of pink orthoclase. It also contains fragments of foreign material.

Between this and the next felsite is a very thin flow of pyroxene andesite which in places is considerably deuterically altered. It only outcrops intermittently in an east-west direction from near Lamb's Valley to Stanhope Creek.

Overlying the John's Hill rhyolite at Lamb's Valley is a lenticular outcrop of pyroxene andesitic pitchstone which forms a hill on the eastern side of Lamb's Valley Road.

Two fairly thin flows of felsite come next in ascending order in the Volcanic Stage. These vary in character and like all the other lavas contain fragmental inclusions. In Dutton's Creek is a phase of the upper flow almost identical with the pink coloured phase containing biotite of the top dacite tuff series.

A thin lower flow of hornblende andesite lies below a thick flow of pyroxene andesite, separated from it by a band of tuff and conglomerate. It is very similar in character to the upper flow described below. It is probably the equivalent of the Martin's Creek type. It is not as persistent in outcropping and disappears to the east just after the upper pyroxene andesite is met. Whether this hornblende andesite continues under the talus from the hills it is impossible to say. Like the upper flow, it too is deuterically altered, and in places it is difficult to recognise the deuterically altered rock as hornblende andesite. When it is a dark reddish brown in colour and the hornblende phenocrysts are almost microscopic it closely resembles some of the earlier felsites. This flow is underlain by a thin flow of hornblende andesitic pitchstone.

The highest ridge of the series of hills to the east of the district is composed of pyroxene andesite. This is the upper flow of pyroxene andesite and has a maximum thickness of about 1,200 feet. The upper part of the flow is glassy and in all probability is a separate flow overlying the lithoidal phase. It is impossible to map a boundary between the two phases. Outcrops of the flow are terminated in portion 104, Parish of Stanhope, by a small hill of pitchstone. The lithoidal phase when fresh is a dark grey in colour and is fairly coarse grained in comparison with the other andesites. The sudden termination of such a thick flow seems strange and may indicate a possible fault but this cannot be so as other beds are continuous. The other solution is that it probably thins out rather quickly towards the west under some high level gravels from Stanhope Creek.

The hornblende andesite overlying the pyroxene andesite also forms part of the hills to the east and in parts it is difficult to distinguish between it and the overlying toscanite, especially when the hornblende andesite contains free quartz. This flow of andesite is fairly thick and is wonderfully persistent. It extends right across the area, turning to the north at Elderslie, where it is faulted by minor tear faults associated with the Hunter overthrust fault. When fresh the hornblende andesite is a bluish black colour with bright glassy phenocrysts of plagioclase and black phenocrysts of hornblende and biotite. The andesite varies in character, for in places it contains an abundance of quartz and would then more suitably be termed a dacite. In places along the flow the andesite has been deuterically altered. Where this has happened the groundmass becomes lighter in colour, often changed to a grey colour, and the plagioclase phenocrysts become whiter. Where the rock is weathered the groundmass is very light, the felspar white and the hornblende has taken on a dull greenish black appearance due to alteration to chlorite. Even in hand specimens one can see the phenocrysts of plagioclase altered to chlorite at the centre. The rock contains inclusions, the amount varying in different parts of the flow. Both this and the lower hornblende andesite flow are parted in a peculiar fashion which gives rise to rather thin blocks resembling flagstones. It is a noticeable fact, however, that where free quartz is fairly abundant the hornblende andesite does not bear this particular type of parting. The acid phase seems to be towards the base of the flow. A glassy phase of the hornblende andesite occurs in places below the lithoidal phase. This pitchstone phase and all the other glassy phases of the andesites are characterised by veins through the rock of red limonite which forms ridges on the weathered surfaces.

Overlying the two flows of the hornblende andesite are thin flows of an andesite rock, probably a keratophyre, which consists of numerous lath-shaped phenocrysts of white plagioclase in a dark purplish coloured groundmass. It appears to weather very easily. The flow above the upper hornblende andesite is more persistent than the one above the lower.

Overlying the hornblende andesite is a flow of toscanite which consists of two horizons separated by a thin band of conglomerate. The toscanite gives rise to the most northern row of hills which extend west from Lamb's Valley. Both horizons disappear about portion 104, Parish of Stanhope, the only trace of the toscanite found elsewhere being along the southern boundary of the top lava flow in the Volcanic Stage further west and at Glendonbrook. The toscanite of each horizon differs slightly, that of the upper horizon being a brownish colour and containing abundant quartz and plagioclase phenocrysts with a little orthoclase and biotite, while that of the lower horizon is a khaki colour, being slightly weathered and containing phenocrysts of quartz and plagioclase. Both are usually streaked with veins of limonite and contain fragmental inclusions.

The topmost bed in the Volcanic Stage consists of a series of "flows" of dacitic pitchstone, dacite tuff and ignimbrites (Marshall, 1935) which outcrop from Lamb's Valley Road across the Stanhope District to Elderslie, where they swing to the north and continue to outcrop to Glendonbrook, where they are cut by the Webber's Creek fault. The total maximum thickness is about 800 feet and is reached near Lamb's Valley Road, where most phases appear to be present. There appears to be at least five phases. The phase at the base is ignimbritic and is not persistent throughout the length of the outcrop but good outcrops occur above the toscanite. Overlying the ignimbrites is a thin flow of dacitic pitchstone which contains a fair abundance of biotite and inclusions of fragments of older lavas. This pitchstone outcrops in a small quarry along Lamb's Valley Road, and near Tangorin. In places it appears to be transgressive into the overlying light pink coloured rock, rich in veins of chalcedony

which appear to be elongated in the direction of flow. Along Stanhope Creek the black dacitic pitchstone is absent, but overlying the basal ignimbrite is a pink rock, different from the rock just mentioned, containing numerous fragments. On microscopic investigation this rock type appears to be a dacite tuff and is probably the fragmental equivalent of the pitchstone. Good outcrops of this rock also occur along Dutton's Creek. The next phase is that which overlies the pitchstone. It is a light coloured rock, white in some places, pink in others. This type is very rich in biotite phenocrysts and contains a few tiny quartz phenocrysts and abundant fragmental remains. It appears to be the devitrified equivalent of the pitchstone. Above this phase is a light fawn coloured rock, probably an ignimbrite, containing abundant fragments and phenocrysts of felspar. It forms a persistent outcrop towards Glendonbrook. The ignimbrite of the topmost phase has a brownish red coloured groundmass and contains abundant white phenocrysts of plagioclase and some biotite. It also contains fragments of other rocks which have become elongated in the direction of flow. This phase outcrops intermittently along the whole length of the flow.

To the west of the eastern portion of portion 104, Parish of Stanhope, the lava flows are separated by bands of varying thicknesses of tuff and conglomerate. In the creek banks good sections of conglomerate can be seen. In all cases the boulders vary in size from a fraction of an inch to about eight feet in diameter. They are all waterworn but no ice scratched pebbles have been found. These boulders are so large and so irregularly sorted and dumped, some being on end, that it seems that they must have been deposited by glacial action. In most cases the matrix is tuffaceous and has weathered rather readily, leaving the boulders irregularly sorted and scattered over the surface. Near Harde's house the fluvio-glacial conglomerate underlying the lower hornblende andesite has a hard tillitic matrix.

The boulders and pebbles vary in composition. For the most part they consist of underlying lavas, cherts, quartzites, aplites and pink granite. The fluvio-glacial conglomerate between the two hornblende andesites which outcrops along the bank of the Hunter River contains numerous boulders of all sizes of hornblende andesite which are held together by what appears to be a very coarse tuffaceous matrix. The matrix is very decomposed.

The tuff varies in texture from fine grained to fairly coarse grained. It is generally pink in colour and consists of fragments of all kinds. It is easily eroded and in the beds and banks of creeks has a curved waterworn appearance. For the most part the tuff is felspathic. Mostly in the Volcanic Stage the tuffs and conglomerates are interbedded and the beds are usually so thin that it is impossible to indicate them on a map or section. They often appear to merge into each other and one gets gradations such as a pebbly tuff and a tuffaceous conglomerate. A peculiar type of conglomerate occurs between the lithoidal pyroxene andesite and the small lenticular outcrop of pyroxene andesitic pitchstone at Lamb's Valley. It is well exposed in a creek on the opposite side of the road to the Post Office. It consists of pebbles of pyroxene andesite and of cherty material set in a matrix of pyroxene andesite. It is probable that an earlier flow of pyroxene andesite had time to consolidate, became disrupted and rounded by water action before another flow, probably from the same fissure, flowed over the water-worn pebbles and caught them up. This pyroxene andesite conglomerate does not continue on the western side of Lamb's Valley Road, its place being taken by the ordinary fluvio-glacial conglomerate so characteristic of the district.

Glacial Stage. The Glacial Stage of the Kuttung rocks is divided into two sub-stages, namely the Lower Glacial Stage and the Upper Glacial Stage, which are separated by a thick flow of toscanite. The Upper Glacial Stage constitutes

the main glacial beds in the district. A general section through the Glacial Stage reveals the following succession :

	Feet
Conglomerate	50
Trachyte flows	100
Varve shales	150
Conglomerate	100
Tuff with <i>Rhacopteris</i>	100
Conglomerate	870
Rhyolite tuff	530
Conglomerate, varves, tillite	530
Toscanite	530
Conglomerate	1,320
Tuff	1,320
Conglomerate	1,320
Total	4,280

Vulcanicity did not cease at the end of the Volcanic Stage as evidenced by the toscanite and rhyolite tuff and the tuffaceous nature of some of the sediments.

The basal bed of the Glacial Stage is one of fluvio-glacial conglomerate consisting of large water-worn boulders of older lavas, pink granite, aplite, quartzite and chert. To the east at Lamb's Valley the conglomerate is characterised by large rounded boulders of grey granite and attains a thickness of about 750 feet. Good outcrops are exposed along Lamb's Creek near the bridge across the road and to the north along either side of Lamb's Valley Road. The most westerly position where the grey granite conglomerate outcrops is along the bank of Sandy Water Holes. Here the grey granite boulders are less numerous, while the boulders of pink granite, aplite and lavas increase in number. At Lamb's Valley the large boulders of the grey granite predominate over a few smaller pebbles of chert, aplite and pink granite. The matrix appears to be fairly coarsely tuffaceous and weathers rather readily. This basal conglomerate is probably the equivalent of the coarse conglomerate which occurs at the base of the Glacial Stage in the Paterson-Clarencetown area.

Overlying this basal conglomerate is a thick bed of pink tuff which for the most part is fine grained and micaceous. It resembles the tuffs of the Volcanic Stage. Interbedded with the tuff is a thin band of cherty tuffaceous rock containing *Rhacopteris*. The pink tuff in places passes into a brownish coloured sandy tuff. Towards the top of the bed the tuff becomes pebbly and passes into a conglomerate.

Above the conglomerate is a thick band of toscanite which has given rise to the steeply sloped range of mountains extending across the district. It is very persistent and resistant to erosion.

Along the Cranky Corner Road one is able to see most of the succession of the beds in the Upper Glacial Stage above the toscanite. Following the toscanite is a thin flow of felsite consisting of phenocrysts of quartz, plagioclase and some biotite in a fawn coloured groundmass. This felsite can be seen on Durham Peak, where it has a slightly different appearance. Here it is a pale pink and green rock with phenocrysts of quartz and orthoclase and has been kaolinized to a certain extent.

Following this felsite are two thin beds of varve shales which are separated by about 25 feet of tillite, tuff and fluvio-glacial conglomerate. The varves are a chocolaty brown colour and are easily weathered as indicated by the small

fragments strewn along the road. The upper band is of the fine sandy type called by Browne "varvoids". Along a tributary creek to Stanhope Creek the "varvoids" are sandier, less weathered, well banded and show contortions in places. It is possible that these are not true varves but are fine banded tuffs and the contortions are due to slumping. To the west near Sandy Water Holes the varves are not seen, but the felsite is overlain by a thick bed of fluvio-glacial conglomerate which contains abundant fossil wood. This conglomerate gives rise to the steep sides of the valley of Sandy Water Holes.

Another thin band of tillite follows, succeeded by a thin bed of rhyolite tuff which is generally pink in colour. This tuff passes into a coarser tuff and then to a green siliceous tuff. Overlying these tuffs is a thick bed of rhyolite tuff which seems to attain its maximum thickness of 700 feet near Cranky Corner. It varies considerably in character, and generally speaking consists of phenocrysts of quartz, both feldspars and biotite in a groundmass which for the most part is kaolinized and varies in colour. Towards the top of the bed the rock becomes megascopically tuffaceous and then passes into a very coarse rhyolite tuff which contains angular fragments of rhyolite, chert and quartz up to about half an inch in width. In comparison with the number of fragments, there appears to be very little matrix. The rhyolite tuff appears to peter out quickly to the west.

The rhyolite tuff passes into a fluvio-glacial conglomerate and then a pebbly tuff. Overlying the conglomerate and tuff is a thin band of tillite. It is light in colour and contains angular fragments in a very hard tillitic matrix. It outcrops along the Cranky Corner Road at Cranky Corner. The conglomerate at Cranky Corner immediately below the tillite contains both rounded and angular fragments which include a fair quantity of varve shales. As no similar varves have been found in the district below this conglomerate, the fragments probably came from further east, where they do occur on a lower horizon.

Next comes a persistent band of cream-coloured varve shales with a maximum thickness of about 150 feet, which in places are contorted. It is overlain by a few feet of fluvio-glacial conglomerate and tillite. The varves thin out quickly in the direction of Cranky Corner. East of Cranky Corner they are underlain by a few feet of conglomerate and then a band of light coloured tuffaceous sandstone which has interbedded with it a very fine white tuffaceous shale containing abundant remains of *Rhacopteris*. This band of tuff continues in a north-easterly direction and is found to contain marine fossils which include *Spirifer striata* (?), *Dielasma* and *Schizodus* and remains of plant stems which are indeterminate.

The tuff appears to thin out towards and disappears at Cranky Corner. However, another tuff which seems to be on the same horizon occurs but contains no fossils. This tuff may be the terrestrial equivalent of the marine tuff. The conglomerate between the tuff and varve shales is fluvio-glacial, and towards the east becomes thicker and more tuffaceous. In parts it is actually a pebbly tuff.

To the east of Cranky Corner is a very thin flow of toscanite which resembles the Paterson type. It is interbedded with the tuffaceous conglomerate between two thin bands of varve-like rock.

Towards the top of the Carboniferous in the district near Cranky Corner and trending north-west and north-east is a thin flow of trachyte which appears to thicken towards the north-east, where it is found associated with a trachyte breccia. There appears to be about three flows of the trachyte as in places the trachyte is interbedded with conglomerate and tillite above the varves as at Cranky Corner and further east with the varve shales, which it seems to have hardened. Of the three flows the lowest is porphyritic, the middle fine grained trachyte, and the top flow amygdaloidal. The fresh specimens are dark grey in colour but weather to a brown rock. The very weathered specimens of the

amygdaloidal type are khaki in colour and the amygdules have either been stained or replaced by brown limonite.

Permian.

The rocks of Permian age were not studied in detail but the following are a few facts noted.

The most important outcrop of Permian rocks in the district is that which occupies the Cranky Corner Basin. Only the beds at the base of the series were noted. The rocks belong to the Lower Marine Series.

The basal bed is very persistent and consists of tuff which weathers to a bluish grey coloured rock. Along the eastern boundary of the Permian the tuff passes into a rather felspathic type. It is a dark grey in colour and contains abundant orthoclase and plagioclase crystals. Marine fossils are found in this tuff and include *Spirifer*, *Martiniopsis*, *Ptychomphalina morrisii* and *Nuculana*.

The next band appears to be the *Eurydesma cordata* horizon. This is a persistent horizon and can be traced along the south-eastern portion of the basin. The bed is a conglomerate and contains countless numbers of *Eurydesma cordata* and some large *Pectens*.

Another outcrop of Permian beds, probably Lower Marine in age, is on the southern side of the Hunter overthrust fault. The series here consists of a band of tuffaceous sandstone containing remains of *Fenestella* and *Ptychomphalina morrisii*.

The Upper Coal Measures are represented along the western side of the Hunter overthrust fault. Some of this series outcrops along the river and for a short distance along the Elderslie Road.

The Permian and Carboniferous strata in the Stanhope District appear to be conformable in spite of the fact that there was a transition from terrestrial to marine sedimentation at the end of Carboniferous time.

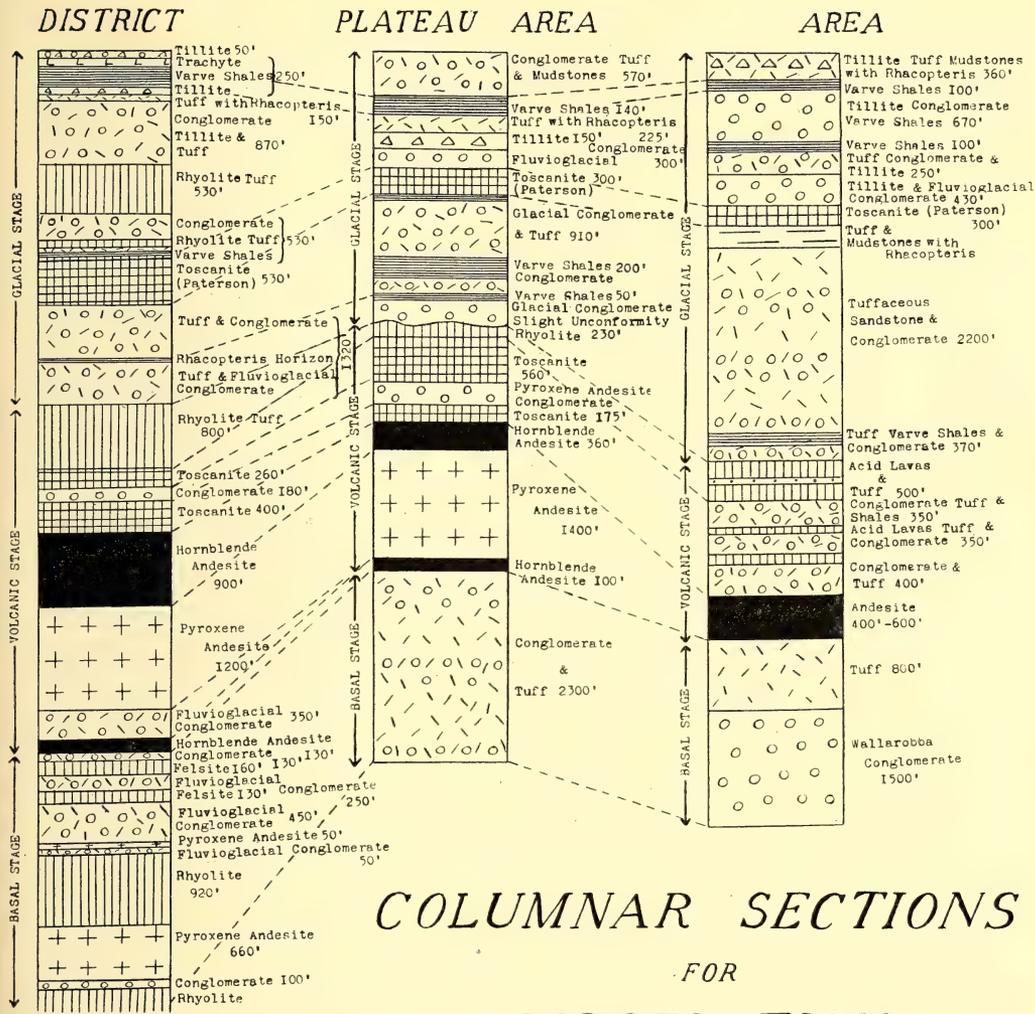
Pleistocene and Recent.

Pleistocene deposits in the Stanhope District are represented by the high level alluvium of the terraces along the Hunter River. These terraces are 100' and 50' above sea level and are regarded as being of Pleistocene age from the occurrence of *Nototherium* remains in them at Elderslie, recorded by Professor David (1907). They consist of alluvium and some pebbly material. At times it is difficult to distinguish between the high level gravel and the loose pebbles from the Kuttung conglomerates, as both contain similar types. The distinguishing feature is that the high level alluvium contains pebbles of red jasper which are not found in the conglomerate. These jasper pebbles have a peculiar weathering effect on the surface, such as small circular cuts. Only remnants of the high level gravels remain in places.

Recent deposits are represented by a cemented rubble which occurs irregularly distributed throughout the area. It consists of pebbles of all types of composition, some of which are rounded, others angular of all sizes cemented into a more or less compact mass which usually has a dirty grey colour. The matrix is porous and crumbly. This recent type of conglomerate is usually level bedded and lies unconformably upon the underlying rocks. Browne (1926) has described occurrences of similar deposits in the Gosforth and Pokolbin districts, and Osborne (1922) in the Paterson-Clarencetown area.

Recent deposits of alluvium in the form of fine sandy silt are to be found on the flood plains on either side of the Hunter River and along some of the creeks.

STANHOPE DISTRICT GOSFORTH-MOONABUNG PLATEAU AREA SEAHAM-CLARENCETOWN AREA



VERTICAL SCALE
1 INCH TO 2,000 FEET

COLUMNAR SECTIONS
FOR
CORRELATION

Fig. 2.

Correlation of Stratigraphy with that of Adjoining Areas.

The two areas used in the correlation of the stratigraphy of the Stanhope District are the Gosforth-Moonabung Plateau area which adjoins it and the type area, the Seaham-Clarencetown area further to the east.

The stratigraphy of the adjoining area corresponds very well with that of the Stanhope District, while that of the Seaham-Clarencetown area corresponds only to a certain extent.

As in the Seaham-Clarencetown area the stratigraphy of the other two areas has been divided as well as possible into the three stages, namely Basal, Volcanic and Glacial. The Martin's Creek hornblende andesite horizon present in the three areas is taken as the base of the Volcanic Stage and the acid lava flow, commonly called a rhyolite, as the top of the stage. The Glacial Stage can be divided in all areas by the Paterson toscanite into the Upper and Lower Glacial Stages.

The Basal Stage of all three areas does not correspond. In the Stanhope District the Basal Stage is represented by a series of lavas separated by fluvio-glacial conglomerates and tuff as in the Volcanic Stage, into which it passes without any change. The Basal Stage in the Gosforth-Moonabung plateau area is represented by a great thickness of tuff and conglomerate and so differs from that of the Stanhope District and also from the Seaham-Clarencetown area, where the base of the Kuttung is represented by a great thickness of conglomerate, the Wallarobba conglomerate, and tuff which contains *Lepidodendron*.

The Volcanic Stage in all three areas compares exceptionally well, particularly the Gosforth-Moonabung Plateau and Stanhope areas. The lava flows seem to attain their maximum thickness in the Stanhope District.

The Glacial Stage was ushered in with a band of fluvio-glacial conglomerate, followed by a series of tuffs which in the Gosforth-Moonabung Plateau and Seaham-Clarencetown areas contain thin bands of varve shales. In the Gosforth-Moonabung Plateau area there is a slight unconformity between the Volcanic and Glacial Stages. The Upper Glacial Stage is represented throughout by a series of fluvio-glacial conglomerates, tillites, varves and tuffs, but in the Stanhope District there has been a greater continuation of volcanic activity which is not represented in the other two districts. This volcanic activity is represented by flows of rhyolite and trachyte. Another feature of the Stanhope District is the presence of a thin band of tuff containing marine fossils.

To summarize, the Stanhope District cannot be satisfactorily divided into the Basal, Volcanic and Glacial Stages and proves that the boundaries between the stages are only arbitrary and only hold for the type area. The stages can only be gained when considering the time factor and indicate that the area was undergoing different conditions at the same time that the other areas were experiencing other conditions, as is expected in a volcanic area. For instance, in the Stanhope District both volcanic and glacial conditions were prevalent throughout the whole of Kuttung times as represented by the lava flows and the fluvio-glacial conglomerates, tillites and varve shales. The type area, however, can in contrast be satisfactorily divided into the three stages as three different types of conditions prevailed. In the Gosforth-Moonabung Plateau area the divisions hold to a certain extent. Here volcanic activity commenced at a later stage than in the Stanhope District and at an earlier stage than in the type area, as the Basal Stage contains a greater thickness of tuffs and towards the top, a flow of felsite.

PETROLOGY.

Petrography.

The petrography of the rocks in the Stanhope District is very similar to that of most of the rocks of the Kuttung from other districts. The rocks vary from

basic intermediate volcanic to acid volcanic and are of numerous types. The three main groups are the andesites, toscanites and rhyolites, which vary within themselves with regard to the percentages of the various mineral constituents.

Petrological problems such as deuteric action involving albitization, chloritization and kaolinization, and devitrification with its allied structures present themselves.

ANDESITES.

The andesites consist of two distinct groups characterized by hornblende and biotite on one hand and augite and hypersthene on the other. Both groups comprise lithoidal and glassy phases.

Pyroxene Andesites.

Glassy Varieties. Megascopically the pyroxene andesitic pitchstones resemble very much the hornblende type described below, with the exception that the pyroxene type contains more plagioclase phenocrysts, which are a creamy colour.

Microscopic investigation reveals that the tabular crystals of plagioclase are the most abundant phenocrysts developed porphyritically in the rock. They are idiomorphic in form and appear quite fresh. The approximate compositions are as follows. The plagioclase of the pitchstone underlying the lowest flow of pyroxene andesite is $Ab_{56}An_{44}$, that from the lenticular shaped outcrop at Lamb's Valley $Ab_{52}An_{48}$, while that of the pitchstone overlying the main pyroxene andesite flow is $Ab_{55}An_{45}$. Pseudo inclusions of groundmass are present in some crystals, also small augite inclusions.

Other phenocrysts of importance are the pyroxenes, augite and hypersthene. These have developed in a subidiomorphic prismatic form. Some of the augite shows simple twinning. The hypersthene shows fairly strong pleochroism and good cleavage. It is slightly greater in amount than the augite.

Hornblende phenocrysts are present only in the pitchstone under the lowest pyroxene andesite, and then they are greater in amount than the pyroxenes. These phenocrysts are subidiomorphic and are of the brown variety.

Magnetite is abundant as inclusions in the plagioclase and pyroxenes as well as in the groundmass.

Apatite crystals vary in size and are present in some of the plagioclase and pyroxene.

The groundmass is light brown in colour and consists wholly of glass. There is evidence of resorption in all the phenocrysts. In the pitchstone associated with the main pyroxene andesite the groundmass shows signs of devitrification, having tiny crystals of felspar in the glass.

Lithoidal Varieties. In the district there are three separate flows of the lithoidal variety. Specimens from these flows differ slightly megascopically. In parts of the lowest flow the andesite resembles that of the upper, whereas in others it appears to have a bright dark groundmass in which the phenocrysts of plagioclase are colourless and do not show up against the groundmass. When altered the rock is a dark brownish colour. The andesite of the second flow varies in character and for the most part is deuterically altered to a greyish colour. The upper flow consists of fairly large phenocrysts of white plagioclase in a dark grey groundmass with smaller phenocrysts of augite.

Microscopically all the lithoidal types are somewhat similar. They consist of abundant phenocrysts of plagioclase and a smaller quantity of pyroxene in a light coloured groundmass.

The plagioclase is in idiomorphic tabular crystals and is andesine $Ab_{59}An_{41}$ in the lowest flow and labradorite $Ab_{48}An_{52}$ in the upper flow. The plagioclase

in the middle flow is completely albitized. It shows zoning by composition, decomposition and inclusions. Twinning according to the albite law is very strongly developed and in some cases both albite and Carlsbad types occur together. Usually the plagioclase is partly decomposed to kaolin and partly deuterically altered to albite, but not as much as in the case of the hornblende andesites. In some cases the plagioclase is altered to chlorite towards the centre. The chlorite in turn is replaced by iron ore. For the most part the inclusions are magnetite, pyroxene and some apatite.

The pyroxene includes both augite and hypersthene in variable amounts, but together are subordinate in amount to the plagioclase. In the lowest flow augite is greater than hypersthene and in the middle and highest flows hypersthene is greater than augite. They form subidiomorphic prismatic crystals. The hypersthene shows rather good pleochroism and cleavage. The augite, on the other hand, is non-pleochroic and often shows good simple twinning. The pyroxene on the whole is rather fresh, only being altered around the edges to a dark brownish green mineral which is probably chlorite. Abundant inclusions of magnetite and apatite are present.

Idiomorphic phenocrysts of hornblende occur in the lowest flow. This hornblende is partly chloritized and in parts seems to have been resorbed to some extent by the groundmass.

Magnetite is abundant in the andesites appearing as phenocrysts and as tiny grains scattered throughout the groundmass, particularly in the lowest flow.

Apatite is found as inclusions and in the groundmass. It is usually idiomorphic in form.

The groundmass is generally cryptocrystalline and does not show any glassy patches. Under high power the groundmass appears to be felspathic and contains patches of green chloritic material which is probably pseudomorphic after some mineral.

Hornblende Andesites.

Glassy Varieties. Megascopically the pitchstone or glassy phases of the hornblende andesites are black rocks with a bright resinous lustre streaked with veins of red hæmatite and limonite. They contain phenocrysts of glassy plagioclase, hornblende and biotite. The pitchstone is very brittle.

Microscopically the rock is porphyritic and consists of phenocrysts of plagioclase, quartz, hornblende, pyroxene including both augite and hypersthene, and biotite in a glassy groundmass. Accessory minerals are magnetite and apatite.

The plagioclase makes up about 60% of the phenocrysts and is andesine $Ab_{68}An_{32}$. It is in the form of subidiomorphic tabular crystals which for the most part are clear and exhibit cracking in two directions. The crystals show slight resorption effects around the edges and in some cases contain pseudo inclusions of the groundmass. Zoning by composition and albite twinning are well exemplified. Inclusions include pyroxene, magnetite and apatite.

Quartz phenocrysts are relatively abundant but are subordinate in amount to plagioclase. They are subidiomorphic and show resorption effects. They show cracking, as does the plagioclase.

The pyroxenes are augite and hypersthene and have crystallized in subidiomorphic prismatic form. They exhibit good cleavage and fracture. Hypersthene is greater in amount than augite.

The hornblende is in subidiomorphic prismatic form and is quite subordinate in amount to plagioclase and is also less abundant than the pyroxenes. It is of the brown variety and shows strong pleochroism.

Biotite is in a very small quantity and is brown, showing very strong pleochroism. It is prismatic in habit.

Magnetite is rather abundant and is found both as inclusions in the phenocrysts and in the groundmass. The crystals are cubic and some show resorption effects.

Apatite is in a small quantity and occurs both as inclusions and in the groundmass. Small basal sections are common, as well as tiny prismatic crystals.

The groundmass is very pale brown in colour and is wholly glassy. In it can be recognized tiny as well as the large phenocrysts of the types mentioned above. It shows flow structure and is streaked in parts by narrow bands of limonite and hæmatite. These bands are not true veins, but stains. The groundmass shows cracking similar to that seen in the plagioclase and quartz phenocrysts.

These rocks appear to be intermediate phases between the lithoidal hornblende andesites and the pyroxene andesites.

Lithoidal Varieties. There are two horizons of the hornblende andesite, a lower and an upper, the former being far thinner. Some phases of the upper flow contain more free quartz, otherwise both are fairly similar megascopically. In appearance the rock variation is the amount of deuteritic action and weathering it has undergone. When fresh the rock is bright black in colour with fresh glassy phenocrysts of plagioclase, hornblende and biotite. The deuteritic effects are revealed in the greyer groundmass and the whiter and duller phenocrysts of plagioclase and duller phenocrysts of hornblende. The very deuteritically altered rock is a fawn colour with dull phenocrysts and in some cases it is a reddish brown colour with smaller phenocrysts. The hornblende andesite also varies megascopically in the proportion of salic and femic minerals. Some abound in both, others in comparison are lacking in one or the other, while still in others the phenocrysts of both are scanty.

Microscopically the hornblende andesite is porphyritic and contains phenocrysts of plagioclase, hornblende, biotite and more often than not quartz. Magnetite and apatite are accessory minerals.

The plagioclase is in the form of idiomorphic to subidiomorphic tabular crystals. Where it is unaltered it appears to be andesine ($Ab_{65}An_{35}$). Some crystals show strong composition zoning and in some cases zoning by decomposition and inclusions. Associated with albite twinning is often the pericline or Carlsbad type. The crystals which have been most albitized have also been partly chloritized towards the centre. In some instances the plagioclase has been completely pseudomorphed by chlorite. The albite has attacked the most basic part of the crystal or along the cleavage planes first. In some specimens the plagioclase is partly altered to kaolin. Most inclusions are of magnetite and apatite.

The hornblende is usually in idiomorphic prismatic form. It is of the green variety and is usually partly or wholly altered to chlorite and/or magnetite or limonite. One example from the lower flow shows the hornblende to be pseudomorphed by calcite surrounded by limonite and in some sections pseudomorphed by limonite.

Quite often biotite is present, and it too is often chloritized and/or replaced by an iron mineral.

Magnetite is abundant throughout and appears as phenocrysts or as inclusions in the phenocrysts of plagioclase, hornblende and biotite. It is also to be found scattered throughout the groundmass. It is possible according to Harker (1935) that much of the finely divided magnetite in the groundmass was derived from the breaking up of the hornblende and biotite during resorption of the groundmass.

Modal quartz is found in a considerable quantity in some rocks and where this occurs the hornblende andesites are more dacitic in character. The quartz usually is subidiomorphic in habit and shows resorption effects. It quite often contains pseudo inclusions of the groundmass and shows evidence of fracture.

Apatite is found as small idiomorphic crystals both as inclusions in the phenocrysts and in the groundmass.

The groundmass is generally cryptocrystalline and in some cases has a tendency to flow structure. In some cases the groundmass has small chloritized patches. Tiny vesicles filled with chlorite and/or chalcedony are frequently found in the groundmass.

Fragments of earlier flows and sedimentary rocks are commonly found in the hornblende andesite and in some instances the fragments represent cognate xenoliths which are actually portion of the first cooled part of the flow.

TOSCANITES.

Toscanites occur in both the Volcanic and Glacial Stages in the district. The two types vary both megascopically and microscopically. In some places the toscanites are more dacitic than toscanitic, depending on the amount of orthoclase present.

The toscanite of the Volcanic Stage corresponds with the Mt. Gilmore type and that of the Glacial Stage with the Paterson type in the Clarencetown-Paterson District (Osborne, 1925).

The toscanite of the Volcanic Stage is found on two horizons, the upper toscanite being a brownish colour and containing abundant phenocrysts of quartz and plagioclase with some orthoclase and a little biotite. It contains fragmental remains. The more weathered specimens are streaked with veins of limonite. The Paterson type is a bluish grey colour becoming brownish on weathering. It contains abundant phenocrysts of quartz, plagioclase and some orthoclase and biotite in a stony groundmass.

Microscopically the toscanites consist of phenocrysts of plagioclase, orthoclase, quartz and biotite in a light brown coloured groundmass.

The plagioclase is the most abundant felspar and is andesine $Ab_{63}An_{37}$. It occurs in subidiomorphic crystals, is partly albitized and kaolinized, and in places is also altered to sericitic material and chlorite. It shows zoning by decomposition.

Orthoclase is present in a smaller proportion than the plagioclase. It has simple twinning and has also been slightly deuterically altered to albite.

Quartz is fairly abundant and occurs in large subidiomorphic crystals which show resorption effects and contain pseudo inclusions of the groundmass.

The ferro-magnesian mineral is biotite, which is present in a small quantity. It is in the form of idiomorphic prismatic crystals. It is very dark in colour and is speckled with magnetite, which has probably been derived from the mineral. It also shows alteration to chlorite in some cases.

Magnetite is not very abundant and occurs as phenocrysts which show signs of resorption. It is altered to limonite in some cases.

Apatite is an accessory mineral and is found as inclusions and in the groundmass.

The groundmass is hypohyaline, being partly cryptocrystalline and partly glassy. It usually shows excellent flow structure and in some cases shows spherulitic structure. The latter feature is well seen in an example of the Paterson toscanite. The spherules are stained with limonite and as a result it is difficult to determine their composition. A tiny crystal of felspar or a tiny fragment of cryptocrystalline groundmass is often found as a nucleus for the crystallization of the spherules. The groundmass on the whole is stained in patches with limonite and contains patches of chloritic material.

DACITES.

Dacites are intermediate in composition between hornblende andesites and toscanites. Although some of the two latter types are dacitic in parts according

to the percentage of quartz and orthoclase present the only true dacite is a biotite dacitic pitchstone which occurs at the base of the top flow in the Volcanic Stage.

Megascopically the rock is black in colour and has a bright pitchy lustre. It contains phenocrysts of biotite and inclusions of other rocks. It is extremely brittle.

Microscopically the rock consists of phenocrysts of plagioclase, quartz and biotite set in a glassy groundmass.

The plagioclase is andesine ($Ab_{68}An_{32}$). The phenocrysts are subidiomorphic and tabular in form and show evidence of resorption. They also show strong albite twinning and composition zoning.

The quartz phenocrysts are subordinate in amount to the plagioclase phenocrysts. They show resorption effects and contain inclusions of the groundmass. It is in the form of subidiomorphic crystals.

Other phenocrysts are of brown biotite which show evidence of strain in the bending of some of the crystals. Evidence of strain is also revealed by cracking by the salic phenocrysts and the groundmass.

Inclusions of idiomorphic needles of apatite are present, also cubes of hæmatite.

The rock contains numerous inclusions which include for the most part pyroxene andesites and fragments of glass. Some of the inclusions show resorption effects and reaction with the groundmass and in some cases are surrounded by a halo of limonite. The inclusions vary in size from a fraction of a millimetre to 2 mm.

RHYOLITES.

The only true rhyolites in the district seem to occur at the base of the series, i.e. the two lowest acid flows. Megascopic descriptions of these types have been given in the description of the stratigraphy.

Microscopically the lowest rhyolite consists of phenocrysts of quartz which show resorption effects in a very light coloured groundmass. The groundmass shows a fine vermicular or imperfect spherulitic effect. Abundant small rounded vesicles filled with granulated chalcedony and calcite occur throughout the rock. Patches of carbonaceous material, probably weathered calcite, are present. The rock resembles a glassy type of rhyolite with vesicles which is becoming devitrified and amygdaloidal.

The John's Hill type appears to consist of phenocrysts of orthoclase and plagioclase which are now almost wholly decomposed to kaolin, albitized, chloritized and in some cases show saussuritization, in a groundmass which is glassy for the most part. Other parts are cryptocrystalline. It shows excellent fluidal fabric and in patches are concentrations of limonite. Where the felspar is cracked, hæmatite infills the cracks. Magnetite occurs as small phenocrysts. Veins of chalcedony are common throughout the rock.

KERATOPHYRES.

The keratophyres which are present in the Stanhope District appear to be andesites which have been completely albitized by late magmatic solutions.

A typical keratophyre occurs above both flows of hornblende andesite. In the hand specimen it is a purplish grey colour with rectangular shaped phenocrysts of plagioclase. Microscopically it is seen to consist of tabular idiomorphic phenocrysts of albite in a cryptocrystalline groundmass. The plagioclase is much altered to kaolin and shows zoning by composition and decomposition. Magnetite is fairly abundant as fine grains and as larger crystals.

TRACHYTES.

The only trachytes in the district occur at the top of the Upper Glacial Stage and outcrop at Cranky Corner and to the north-east of it. They appear to occur in three flows; the lowest is porphyritic and is purplish grey in colour and contains larger phenocrysts of plagioclase. It is more in the nature of a trachyandesite.

Microscopically the porphyritic stage consists of phenocrysts of plagioclase and a few of augite in a groundmass of tiny tabular crystals of felspar which give rise to a trachytic fabric. The phenocrysts of plagioclase are tabular idiomorphic crystals which have been completely albitized. The augite is in subidiomorphic prismatic crystals and in places has been silicified. Magnetite is fairly abundant. The groundmass consists of tiny idiomorphic crystals of felspar which for the most part is orthoclase and some plagioclase. Both have been somewhat albitized. The orthoclase crystals show simple twinning. The crystals in the groundmass give rise to a trachytic fabric. Tiny vesicles in the rock are filled with chlorite and chalcedony.

The middle flow consists of a greenish grey fine-grained trachyte. A section of this fine-grained trachyte shows good trachytic fabric and consists of tiny tabular shaped crystals which have been partly albitized and chloritized. The felspar crystals vary in size and show simple twinning. Chlorite is interstitial. Abundant cubic crystals and grains of magnetite are present. Apatite is present in a very minute quantity. Carbonaceous material is scattered about in the groundmass. The rock has been much deuterically altered.

The top flow of the trachytic series is amygdaloidal, the amygdules consisting of chalcedony, calcite, chlorite and zeolite. The fresh rock is a greenish grey in colour and weathers to a dark reddish brown type and on further decomposition to a khaki coloured rock in which the amygdules are stained or replaced by limonite. The rock in parts is quite vesicular.

Microscopically the rock consists of phenocrysts of plagioclase, hornblende and some augite in a groundmass composed of tiny crystals of plagioclase, orthoclase, augite and iron ore. The plagioclase is in idiomorphic lath-shaped crystals and is of two sizes, the larger as phenocrysts and the smaller taking their place in the groundmass. The plagioclase has been completely albitized and in a few instances is partly chloritized towards the centre. It is impossible to determine the original type of plagioclase.

Hornblende is the next abundant phenocryst, and is very subordinate to the felspar. Some pieces are partly chloritized. It is in subidiomorphic form.

Pyroxene, hypersthene, gives rise to a few small phenocrysts and is in subidiomorphic form. This mineral forms tiny grains in the groundmass.

Other constituents in the groundmass are iron ore, which is quite abundant, and probably orthoclase. It is very difficult to definitely recognize orthoclase from plagioclase in the tiny crystals on account of the great amount of albitization. The rock contains numerous vesicles which have been infilled by secondary material, giving rise to an amygdaloidal rock. These secondary materials have been named in the megascopic description of the rock.

DACITE AND RHYOLITE TUFFS.

These tuffs are to be found on several horizons. Megascopically they resemble rhyolites.

Thin bands of dacite tuffs occur in the Volcanic Stage. The best and thickest development of them is associated with the dacitic pitchstone at the top of the Volcanic Stage.

Megascopically the tuffs are pink in colour and contain phenocrysts of biotite and fragments of foreign material.

Microscopically the rocks consist of phenocrysts of plagioclase, quartz and biotite in a groundmass of cusped fragments of devitrified glass. These fragments are stained with limonite and are welded together. Inclusions of basalt, shale and unstained glass appear in the groundmass.

The rhyolite tuffs can be divided into two groups, the first being characterized by a greater proportion of plagioclase than orthoclase and the second by those in which the amount of orthoclase is greater than plagioclase. The two upper bands of rhyolite tuff in the Glacial Stage are typical of the latter group, while the top rhyolite tuffs of the Volcanic Stage and the lowest rhyolite tuffs in the Glacial Stage are characteristic of the first.

Sodipotassic Rhyolite Tuffs.

The megascopic characteristics of these rocks have been briefly described in the stratigraphy. Microscopically these tuffs are composed of phenocrysts of quartz, plagioclase and some orthoclase and sometimes a little biotite in a groundmass which is usually glassy and shows signs of devitrification.

The quartz usually shows resorption effects and contains pseudo inclusions. The feldspar is generally albitized to a certain degree and kaolinized. Plagioclase is in a greater proportion than orthoclase and is acid oligoclase. The groundmass is generally kaolinized and is stained with limonite. It shows good flow structure.

Potassic Rhyolite Tuffs.

As stated above, the rhyolite tuffs which come under this heading are those forming the two upper flows in the Glacial Stage. The megascopic characters of the rocks have been briefly given in the stratigraphy.

Microscopically the potassic rhyolite tuffs contain abundant phenocrysts of quartz and feldspar, the greater part of which is orthoclase, and some biotite in a groundmass which shows signs of devitrification.

The quartz is usually in subidiomorphic prismatic form, shows resorption effects, and often contains pseudo inclusions of the groundmass. Sometimes the quartz is in angular fragments which also show resorption effects.

The feldspar most predominant is orthoclase, which is usually altered to a greater or less extent to kaolin and is often stained with limonite. Some crystals show simple twinning. Plagioclase is less abundant and when present is usually in small crystals and shows albite twinning. Both feldspars are somewhat albitized.

The groundmass of these rhyolite tuffs is usually kaolinized and stained with limonite. On the whole it usually shows excellent flow structure and consists of cusped fragments of glass and feldspar. The structure of the groundmass seems to indicate a collapsed pumice. See Figure 3 A and C.

Ignimbrites.

Although these rocks are a type of rhyolite tuff, microscopically they have a slightly different aspect from the characteristic type of rhyolite tuff prevalent in the district. They occur at the top of the Volcanic Stage and some of the lower felsites in this stage are actually ignimbrites. Megascopic descriptions have been given in the description of the stratigraphy.

Microscopically this type consists of phenocrysts of quartz, plagioclase which is oligoclase ($Ab_{20}An_{30}$) and orthoclase, with a little biotite in a groundmass. The groundmass is composed of abundant shreds of glass and feldspar welded together, and shows flow structure. See Fig. 3B. It sometimes shows comb and spherulitic structures. Furthermore, it is usually kaolinized and in parts stained with limonite. Often fragments of other volcanic rocks and glass are present.

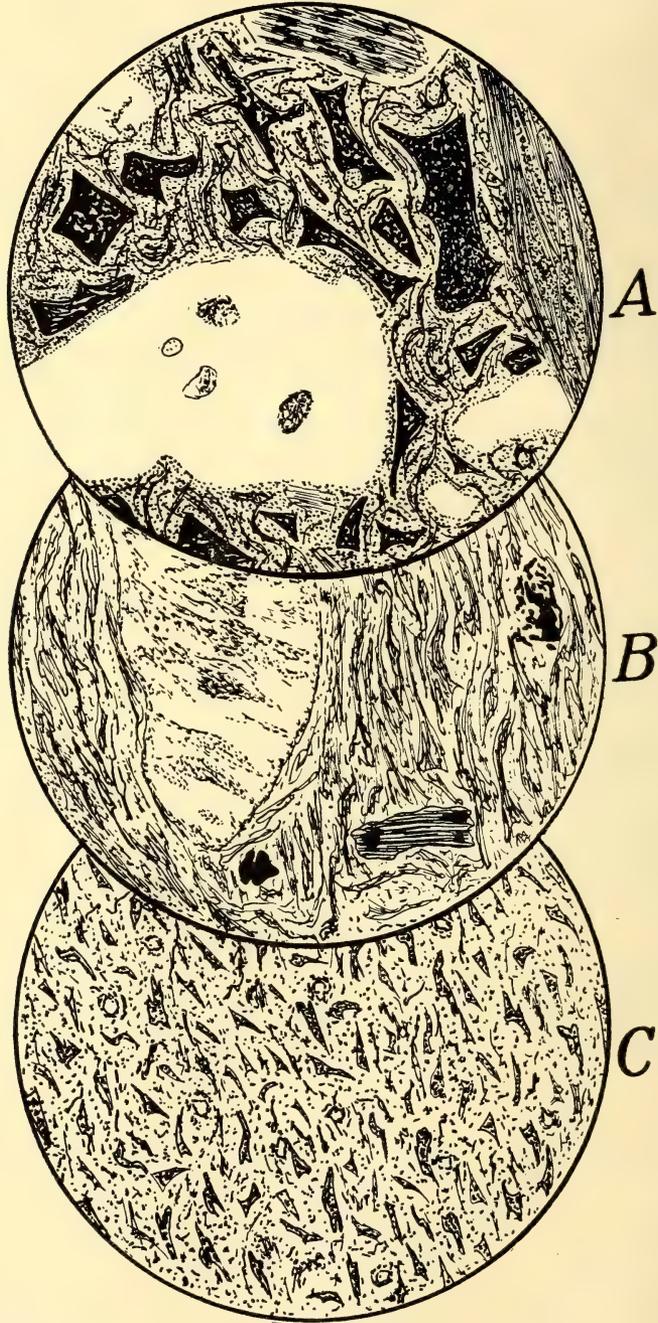


Fig. 3.

- A. Rhyolite Tuff. $\times 30$.
B. Ignimbrite. $\times 25$.
C. Rhyolite Tuff. $\times 70$.

TUFFS (OTHER THAN RHYOLITE TUFFS).

The tuffs of the Volcanic Stage are for the most part pink in colour and are very felspathic. They vary in grain size from extremely fine to moderately coarse. The fragments consist of quartz, plagioclase, orthoclase, biotite and tiny dark fragments of rock. Some fragments are much larger than others and are up to half an inch in width. Other tuffs have a purplish colour and contain abundant fragments of white plagioclase, pink orthoclase, quartz, biotite and other rock fragments. These seem to occur more above the hornblende andesites, whereas the pink ones are above the felsites.

The tuffs of the Glacial Stage are also very felspathic and in places are extremely siliceous and micaceous. They vary in colour from pink to light brown, and may be either very tough or quite friable. A green siliceous felspathic tuff is fairly common but does not give rise to very thick bands. Microscopically a typical example of a pink tuff contains abundant small angular fragments of quartz and feldspar which is decomposed for the most part and an abundance of limonite. The matrix is kaolinized. The pink colour of the tuffs is due to the presence of hæmatite and limonite.

At the top of the Upper Glacial Stage associated with the trachyte flows is a trachyte breccia which consists of angular fragments of trachyte of varying sizes. This is the only true breccia which was found in the district.

THE EFFECTS OF LATE MAGMATIC SOLUTIONS.

Three types of magmatic or deuteritic alteration, namely albitization, chloritization and deuteritization, are prominent in the Kuttung lavas in the district.

Albitization.

The albitization of the feldspars in the Carboniferous lavas in the Stanhope District could well be used to illustrate the paper by Bailey and Grabham (1909) in which they ably expressed their views on the albitization of plagioclase feldspar. Browne and White (1926) describe the albitization of the Blair Duguid hypersthene andesite, a Kuttung lava, and record albitization as having been produced by cognate solutions during the last stages of crystallization.

It was found that the hornblende andesites, toscanites and rhyolite tuffs were the most albitized and the pyroxene andesites were only partially albitized. On the other hand the pitchstone phases of the andesites are relatively free from deuteritic action. This is probably due to the fact that the solutions were unable to percolate through the glassy groundmass. It is found that the albite generally attacks the edges of the crystals and works its way along the cleavages. In some cases the feldspar has been completely albitized, while in others it has been only partially replaced. It is a noticeable fact that the albite attacks the most basic feldspar first. For instance the phenocrysts which are the first to form and so more basic than the minute crystals of the groundmass, are attacked first. Also in zoned crystals the most basic zones, noticeably those towards the centre, are attacked first. This fact helps to point out that the soda effecting the albitization belonged to the magma itself, as the pyroxene andesites which are the most basic rocks in the area are least deuteritically altered. If the effect was due to meteoric solutions then the plagioclase of the pyroxene andesites would have suffered to a greater extent.

In some cases associated with the albite are tiny flakes of sericitic material which is probably a weathering product of the albite. The albite appears to have a rough surface due to the aggregation of the tiny particles of albite and possibly other material which is replacing the plagioclase. Mostly the change takes place molecule by molecule, and as a result the optical properties of the

original plagioclase remain. If the replacement is not complete it may be possible to determine the nature of the original residual plagioclase.

More often than not in the rhyolite tuffs the orthoclase feldspar has been replaced in a patchy fashion by the albite and has a dirty yellowish brown appearance due to iron staining. This staining of the albite is particularly noticeable in the cusped fragments of orthoclase in the pumiceous groundmass.

Chloritization is very often associated with the albitization and this phenomenon helps to indicate that the solutions which effected the albitization were cognate and not meteoric.

Chloritization.

In the Kuttung lavas in the district chloritization as well as being associated with the albitization of the plagioclase is also associated with the ferro-magnesian minerals. Hornblende is especially susceptible to chloritization, also biotite, whereas pyroxene is generally only altered about the edges. In some cases where chlorite has pseudomorphed the hornblende, calcite is in association. This is probably due to the lime separated from the hornblende during the replacement by chlorite. In a section of a rock from the middle pyroxene andesite flow where the ferro-magnesian, probably a pyroxene from the crystal outline, has been pseudomorphed by chlorite, calcite is quite abundant. It is unusual to see the pyroxene so altered to chlorite.

Although chlorite may also be associated with ordinary weathering, an examination of the rest of the rock will usually indicate its origin, as deuteric effects are also usually suffered by the plagioclase. The chlorite replaces the plagioclase towards the centre and sometimes along cleavage planes. Where chloritization is closely associated with albitization its origin may safely be regarded as due to late magmatic solutions.

Patches of chlorite in the groundmasses of the andesites seem to indicate a replacement of some indeterminate material.

Kaolinization.

In spite of the fact that kaolinization is mostly a weathering product, in the Kuttung lavas it must also be regarded as a phenomenon resulting from late magmatic solutions. The groundmasses of most of the rhyolite tuffs have been kaolinized and also the feldspar phenocrysts to a certain extent. Certainly some of the kaolinization is due to ordinary weathering, but not all, the other being due to late magmatic origin. Often the kaolin is stained with limonite and is a yellowish brown colour.

DEVITRIFICATION.

Devitrification has occurred in a great number of the volcanic rocks in the district.

Evidence of devitrification is in a number of forms such as spherulitic and axiolitic structures and alteration of the glass into cryptocrystalline material in a patchy fashion. The rhyolite tuffs show excellent examples of devitrification. The groundmass contains pumiceous material which was originally glassy but has now been wholly or partly altered to cryptocrystalline material. In some of the rhyolites and toscanites the groundmass contains patches of cryptocrystalline material in the glass which can definitely be distinguished from the streaks of glass in some of the other volcanic rocks. The latter case is not due to devitrification but to the fact that the glass did not crystallize out with the rest of the rock due to the heterogeneity of the magma after the phenocrysts had crystallized.

Spherulitic and axiolitic structures are present in some of the toscanites, rhyolites and rhyolite tuffs. The spherules can only be seen microscopically

and show up best in crossed nicols. They appear to be radiating fibres of felspar with possibly some quartz which often show a tiny felspar crystal or a tiny portion of crystalline groundmass as a nucleus. Axiolites do not consist of radiating fibres but of fibres more or less arranged in a parallel fashion. Whereas crystallization commences from a point in spherulitic structure, it commences along a line in axiolic structure.

Bonney and Parkinson (1903) described two types of devitrification, one primary and one secondary. They mention that axiolic structure and some spherulitic structures are indicative of primary devitrification and the patchy type of secondary devitrification. From the evidence available in the Stanhope District it appears as though both are present, sometimes alone and sometimes secondary superimposed upon primary. Bonney and Parkinson, however, fail to give the times of the two types of devitrification but according to Osborne (1925) Bonney, in another paper, indicated that the primary devitrification occurs during cooling and the secondary type long afterwards. In the lavas examined there is little evidence to indicate when devitrification occurred. It is possible that some of it at least may be connected with the activity of late magmatic solutions.

The cause of devitrification is another moot question. Anderson and Radley (1915) agree that there are two types of devitrification and have postulated the following theories for their formation. In primary devitrification where the limits are sharp the process is due to the escape of water very soon after solidification while the rock was still warm. Secondary solidification according to them is due to the later and very gradual penetration of water or possibly other reagents which they do not state. Bonney and Parkinson consider that for primary devitrification the following physical conditions are required—a low pressure with active water content, an initially high temperature and rapid fall. Parkinson suggests that secondary devitrification begins by hydration of the glass in the neighbourhood of perlitic cracks.

In dealing with devitrification a question arises as to whether the lithoidal andesites are the devitrified equivalents of the glassy andesites. As no chemical analyses have been carried out it is impossible to determine the chemical relationship between the two varieties. However, field evidence suggests this is not the case and that both varieties form distinct flows. In the field one would expect to find gradations from glassy to lithoidal types but this is not the case as the glassy phase passes abruptly into the lithoidal phase in all the flows concerned. Also microscopically, if the lithoidal is the devitrified glass, then one would expect to find microscopic evidence in the form of residual glass in the groundmass. On the contrary, no residual glass has been found in the groundmasses of the lithoidal types. It seems, therefore, that the lithoidal types are quite independent of the glassy types.

VOLCANIC HISTORY.

The Carboniferous period, particularly during Kuttung times, was one of the greatest periods of volcanic activity, and great thicknesses of volcanic lavas and tuff were ejected. Two types of volcanic action are evident in the district. In the first place, there are the lava flows which have poured quietly over the surface represented by the andesites, toscanites and rhyolites, and secondly the explosive type represented by the ignimbrites, rhyolite tuffs and other tuffs.

No evidence of a centre of eruption is present in the district, but from the nature of the outcrops of the lava flows the centre of eruption appears as though it was towards the north-east of the district.

During the earlier stages of the volcanic history the eruptions must have been alternately of the quiet and explosive types, the former represented by the lava flows and the latter by the accumulations of volcanic tuff found in between

the flows. Volcanic action in the latter part of Kuttung times was mostly of the fragmental type, as represented by the rhyolite tuffs, as the only important flow is that of the Paterson toscanite.

Accompanying the volcanic activity was glacial action which enabled much of the volcanic ash to be carried along by the glacial streams. Lava flows and tuff were poured out over the glacial and aqueoglacial accumulations, as it is quite common to see beds of tuff or of lava flows immediately overlying the fluvio-glacial conglomerate, tillites and varves.

The true lava flows are more basic in character than those rocks resulting from the explosive type of eruption. They have flowed over the land surface gathering as they went fragments of underlying material. If the flow was of an intermittent nature the surface sometimes cooled quickly and pressure from the lava, when it began to flow again, often caused the crust of the flow to be broken up and caught up in the lava. Evidence of this is seen in the hornblende andesites. It is only natural to expect that these cognate xenoliths and fragments must have caused a certain amount of contamination when they were assimilated or partly assimilated by the lava. Evidence of steam or gas holes, formed when the gaseous substance escaped, is present in the form of vesicles which in most cases have become filled with secondary material.

The ignimbrites according to Marshall (1935) are deposited from immense clouds or showers of intensely heated but minute fragments of volcanic magma. The temperature of these fragments is thought to have been so high that they were viscous and on reaching the ground adhered together and formed a "lava" which was capable of flowing.

The rhyolite tuffs found in the Upper Glacial Stage indicate explosive types of eruptions as they contain numerous cusped fragments of glass which are sometimes devitrified and welded together. These rhyolite tuffs are characteristic of collapsed or broken pumice. The embedded crystals of quartz and feldspar present in most types were formed earlier in the magma reservoir before eruption. These tuffs have evolved from a very acid magma which, after having been shattered in the air, was capable of flowing after having been welded together on reaching the surface. The rhyolite tuffs differ from ignimbrites, the latter having uniform and normally fine texture, while the former are coarser and more fragmental.

The trachyte flows, the last lava flows in the Kuttung, probably originated from a different vent which may have been situated in the vicinity of the trigonometrical station just east of Cranky Corner as here is to be found an abundance of coarse trachyte breccia, and it is here that the flow seems to attain its maximum thickness.

MINERALOGICAL AND GENETIC RELATIONSHIP.

Generally speaking the whole series of volcanic rocks of the Kuttung in the district is fairly acid, the types not containing free quartz are the pyroxene andesite, which is the most basic, and the alkaline trachytic type at the top.

The types of plagioclase feldspar gradually increase in acidity from labradorite $Ab_{48}An_{52}$ in the pyroxene andesites to oligoclase $Ab_{73}An_{27}$ in the sodipotassic rhyolite tuffs. As considerable albitization has taken place, it is not possible to say whether any primary albite occurs in the rocks. The albitization also makes determination of the plagioclase difficult.

The potash feldspar, orthoclase, is absent from the andesites but makes its appearance in the toscanites and the sodipotassic rhyolite tuffs above the toscanite. In the latter orthoclase is greater in amount than plagioclase. The trachyte consists almost wholly of orthoclase.

The ratio of ferro-magnesian minerals to salic minerals in all types is small. It decreases from basic to acid types. Biotite is the most widespread of the ferro-magnesian minerals.

Augite and hypersthene, apart from occurring in the pyroxene andesites, are not found in other types with the exception of the hornblende andesitic pitchstones where they occur with the hornblende. A little has also been found in the andesitic phase of the trachyte.

Iron ore, which consists of magnetite and ilmenite, is fairly abundant throughout, as is apatite.

The mineralogical relationships seem to indicate that the lava flows with possibly the exception of the trachyte are magmatically related.

As no plutonic rocks related to the volcanic rocks have been found in the district nothing can be said of the type of primary differentiation. Iddings (1896) records Brögger as saying that even after portions of the magma have been separated from the parent magma by being erupted into deep-seated parts of the earth's crust, further differentiation may take place in these portions producing basic and acid rocks which may be extruded upon the surface of the earth. A series of eruptions from one of these portions would therefore not be the same as a series from the original magma basin. This indicates that the order of eruption of extrusive rocks is for the most part dependant on relatively secondary differentiation. From field and mineralogical observations of the volcanic rocks in the district it appears as though the parent magma was in the nature of a hornblende andesite from which differentiated more basic and more acid types.

It is possible that the trachyte flows could have originated from the same magma chamber as the calcic types, being the alkaline fraction which was extruded through the same or a different vent from the calcic lavas.

STRUCTURAL GEOLOGY.

Folding.

The basin structure in the area under discussion is shown by the dips indicated along the various flows and beds and the direction of outcrops of the beds. It is also well indicated by the physiography described above.

The beds of the Volcanic Stage do not turn to the north towards the east but continue in a south-easterly-north-westerly direction and form part of the Lochinvar anticline. The amount of dip of the beds on the whole is fairly constant, varying for the most part between 30°-40°. The Permian rocks which have given rise to the Cranky Corner basin have been deposited conformably upon the Kuttung rocks.

The basin in the Stanhope District, known as the Cranky Corner Basin, is separated to the east from the Moonabung Basin, described by Osborne (1927), by a plunging anticline out of which Lamb's Creek has carved its valley. This anticline is really the northern part of the Lochinvar anticline and pitches to the north. The northern portion of the basin has been faulted against the Mirannie Basin, described by Osborne (1926), by the Webber's Creek fault. Osborne (1926) considers that the Cranky Corner Basin may be a faulted portion of the Mirannie Basin, that is both being portions of a large basin which existed before the Webber's Creek fault. He accounts for the relative positions of the two basins at the present time by lateral movement either in an easterly direction on the Cranky Corner side or in a westerly direction on the Mirannie side during faulting. In the south and south-west corner the basin is cut by the Hunter overthrust fault as well as by smaller minor faults.

There is no evidence in the area examined as to the exact age of the diastrophism apart from the fact that it is post-Permian, probably at the end of Palæozoic time, as the Permian beds are conformable upon those of the Car-

boniferous and appear to have been folded with them. According to Osborne (1929) in the Paterson-Wallarobba and Scone Districts there are outliers of Tertiary basalt overlying the remnants of a peneplain which was carved out of the folded and faulted Kuttung and Burindi rocks indicating that the folding and faulting are older than the basalt. From his study of the relationship between the Triassic and Permian formations to the south, David (1907) states that the folding began in Upper Marine times and was completed before the deposition of Triassic sediments.

Faulting.

Faulting is an important structural feature in the Hunter River District. The folded structures which antedated the faulting have been cut by numerous faults. In the Stanhope District the largest and most important faults are the Hunter overthrust and the Webber's Creek fault. In this area the Hunter overthrust fault was originally considered to consist of two parts, the Lachnagar and Elderslie faults. It trends in a general north-west-south-east direction along the Hunter River and then cuts across the Kuttung lavas until it meets Dutton's Creek. It is here dislocated by a smaller fault and is found again near the Hunter River, whence it trends in an east-west direction to Elderslie, where it is again dislocated before turning to the north. From here it trends in a northerly direction until a little before reaching Brook's Mountains, when it trends north-west, continuing in this direction until it meets the Bridgeman-Webber's Creek fault. The Webber's Creek fault has been described by Osborne (1926).

Towards Elderslie are a few minor faults, probably tear faults in the weakened portion of the earth in the vicinity of the major fault.

In the Stanhope District there is no evidence to indicate the nature of the fault, but evidence available elsewhere indicates that the Hunter overthrust fault has a throw of approximately 5,000 feet. This fault has caused Permian strata to be thrust against the Kuttung rocks.

Throughout the whole area slickensides are predominant, indicating earth movements. These are especially noticeable along the Cranky Corner Road, but there is no other evidence such as a break in the continuity of the beds to indicate a major displacement such as a fault.

The faulting is younger than the folding. Its age can be set between two limits, the upper limit being set at pre-Kosciusko Uplift as faulting did not take place during this uplift. If it had, the faulting being of such a magnitude, would have revealed itself by fault scarps, none of which are present in the district. The only relationship between the physiography and the faults is that the streams have sought out the planes of weakness along which to carve their valleys, and resistant Kuttung lavas have been brought up against softer Permian rocks. The lower limit of their age is just after the age of the folding.

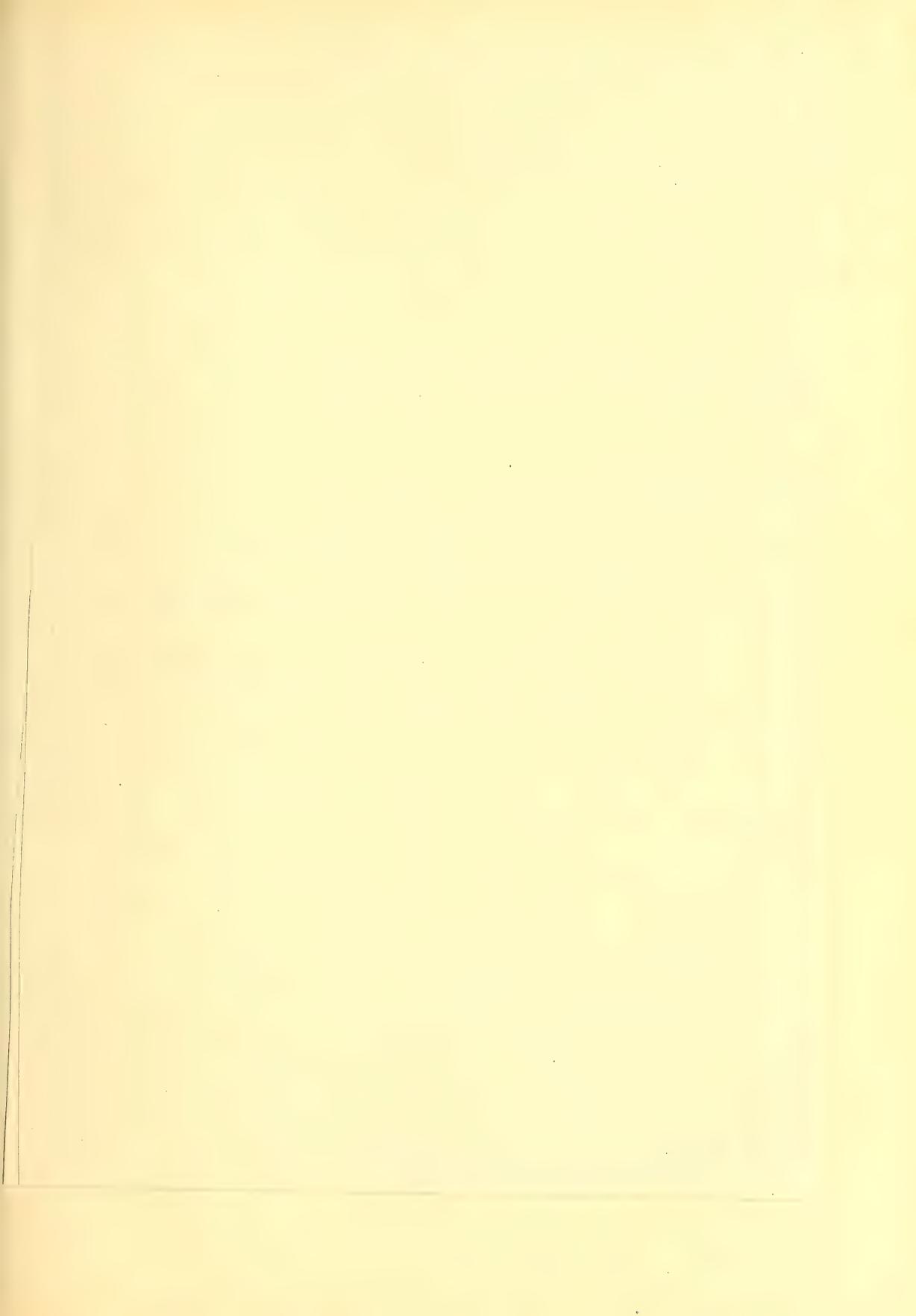
SUMMARY.

The rocks of the Stanhope District are of Kuttung and Permian age and have been folded into a basin structure at the close of the Palæozoic era.

A great thickness of volcanic and glacial beds constitutes the Kuttung. It has been decided that, unlike the type area, the Kuttung rocks cannot be satisfactorily divided into the Basal, Volcanic and Glacial Stages, as both glacial and volcanic conditions were persistent throughout.

The Permian rocks near Cranky Corner rest conformably upon the Kuttung rocks, while those to the south and the west of the area have been brought up against the Carboniferous strata by the Hunter overthrust fault.

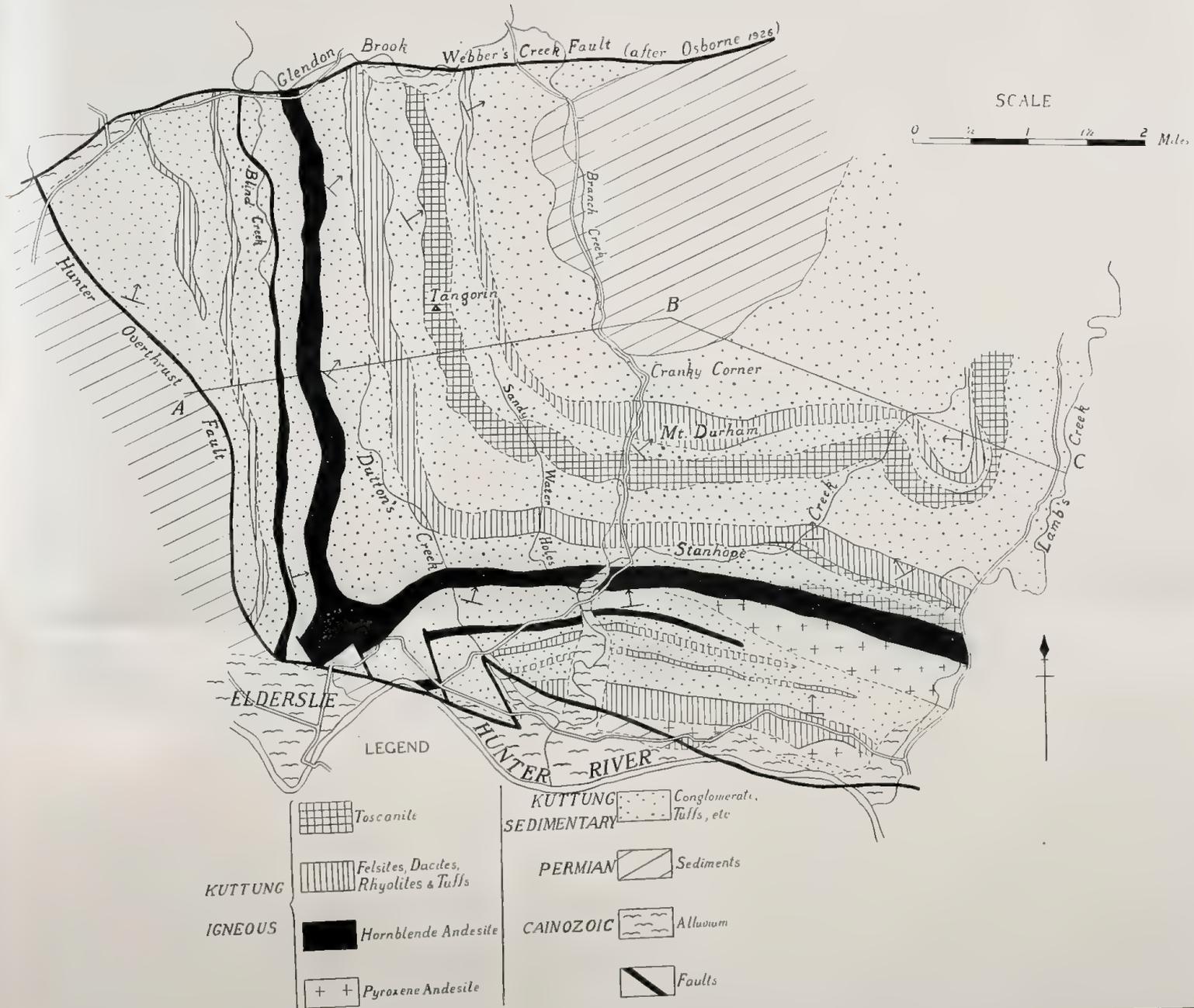
Brief petrographical descriptions of the rock types have been given, and from a study of these it is found that the rocks vary from acid to basic volcanic



GEOLOGICAL SKETCH MAP

OF

STANHOPE DISTRICT N.S.W.



and are related magmatically. They have been ejected by two different types of volcanic activity. From field and mineralogical observation it appears that the parent magma was in the nature of a hornblende andesite which differentiated into acid and basic phases.

ACKNOWLEDGEMENTS.

In conclusion, the writer wishes to express her appreciation of the hospitality and kindness tendered to her during her trips to the area. She would particularly like to mention the kindness of Mr. and Mrs. M. H. Standen of Stanhope, and Mr. and Mrs. P. Grainger and family of Glendonbrook. She is also indebted to Dr. G. A. Joplin for her kind criticism and helpful suggestions in the preparation of the manuscript.

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THE GENERAL GEOLOGY OF THE BOMBALA DISTRICT, N.S.W.

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With Plate VI and three text-figures.

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I. INTRODUCTION.

The town of Bombala, situated on the Monaro Tableland, 330 miles by rail south from Sydney, is the centre of one of the prosperous sheep and cattle raising districts for which the Monaro is famous.

There is no record of any previous geological work in the area, except that it is represented on the state geological map as consisting of Devonian sediments and of granite, with a capping of basalt to the north and south of the town.

Extensive geological studies were carried out around Cooma, over 50 miles north of Bombala, by Browne (1914 and 1943) and by Joplin (1942 and 1943), while nearly 40 miles to the east investigations on the Devonian rocks have been made by Brown (1931). At Quidong, 16 miles south-west of Bombala, Silurian

sediments carrying a considerable fossil fauna have been recorded (Carne and Jones, 1919) but no detailed mapping or collecting has been done in this area. Sussmilch (1914) also makes brief reference to the extensive development of basalt between Cooma and Bombala.

An account of the general geology of the area will be given here.

II. GENERAL GEOLOGY.

The area examined includes a tract of country of some 70 square miles in which an interesting variety of rocks has been found. These comprise unfossiliferous sediments of Ordovician and Devonian age, the former having suffered a low grade of regional metamorphism and in places a superimposed contact metamorphism. No Silurian sediments occur within this specific area, but to the south-west they occur unconformably above the Ordovician rocks and carry a prolific fauna. Tertiary river gravels are common and are frequently overlain by basalt, which covers large areas to the north of Bombala as well as isolated patches to the south. Most of the basalt in the south has now been eroded, only a few small peaks being left as residuals surrounded by more widespread grey billy.

Igneous rocks of both plutonic and hypabyssal types occur, the former as parts of a composite batholith and the latter as dykes. The hypabyssal rocks are grouped around two principal centres—one within the limits of the town itself and called for convenience the "Hospital Porphyries", and the other some three miles to the west, forming the prominent Paradise Hill and penetrating the surrounding rocks in dykes for distances up to three miles. Both these masses are in part garnetiferous.

There are three principal plutonic types forming distinct masses—a coarse acid granite (the Bukalong Intrusion), a granodiorite (the Coolumbooka Intrusion), and a quartz mica diorite (the Bombala Intrusion). Within the Bukalong complex are a number of rock types, some of which are undoubtedly contaminated. The Bombala and Bukalong intrusions have been mapped in detail but only the southern tip of the Coolumbooka mass has been included and its full extent is unknown. The detailed petrology of the igneous rocks will not be attempted here.

III. SEDIMENTARY AND VOLCANIC ROCKS.

The sedimentary rocks are of three ages—Ordovician, comprising steeply-dipping "slates", as they are locally called, an overlying series of gently-dipping Devonian conglomerates, grits, sandstones and shales, and a third group of Tertiary sediments of more limited extent.

(a) *Ordovician.*

Rock Types.

The nature of the sediments which make up the Ordovician strata is variable and includes all gradations between fine pelitic sediments (Joplin, 1942) and coarse sandy and gritty psammitic beds. A considerable number of these are apparently tuffaceous in character. In the western part of the area a few narrow bands of black slate have been found. One of these is a highly pelitic type, the other is more psammitic. These strongly resemble the graptolite-bearing slates of the Cooma district, which are considered by Joplin (1945) to be of volcanic origin. Graptolite-bearing black slates of similar age (Upper Ordovician) are also recorded some 25 miles south-west of Bombala at Tingaringi and Currowang (Hall, 1902). A band of siliceous slate about two feet thick occurs beside the Bibbenluke Road some two miles from the town. It is dark and chert-like in appearance and thin section suggests that it formerly carried

radiolaria, but these are now unrecognizable. Most of the rocks within the area mapped have suffered a certain degree of contact metamorphism with the production of hornfelsed and spotted types.

Structure.

The structure of the Ordovician strata is difficult to determine, as it is impossible to follow an individual bed for any distance. The rocks are gently folded over most of the area, and small-scale faulting is seen in places. This is frequently accompanied by the development of slate-breccias along the fault planes. Minor folds and faults of hand-specimen dimensions are also found. Jointing is strongly developed and the tendency of the rocks to cleave along directions other than the bedding plane increases the difficulty of structural mapping. Folding is commonly seen in the strata, especially in the river sections, the width across the folds being usually of the order of 200 to 300 yards. The surface outcrop of one such fold is seen on the southern side of the Coolumbooka River at the Reservoir. The whole structure may be simply a series of these minor folds, but their irregularity and variation of axial direction suggest that they are rather a cross-warping upon a major structure. At Cooma the general strike of the Ordovician rocks is a little west of north. Here the strike directions are somewhat variable, but the general trend of the main axis of folding also seems to be in a direction west of north. The rocks on the whole are not steeply inclined, the angle of dip averaging about 40° to 50° . No strike and dip readings have been recorded on the map (Plate V) since it is felt that isolated readings could not give a true picture of the structure.

Correlation.

The fact that these slates occur unconformably below the Silurian beds at Quidong, together with their similarity to Upper Ordovician sediments in other areas, and especially their proximity and similarity to those at Cooma, places them almost without doubt as Upper Ordovician in age. The very finely cleaved pelitic rocks are almost identical with some of the low-grade Cooma pelites, and sandy and banded types also resemble some of the Binjura beds at Cooma. On the whole, however, these sediments are not typical of the Binjura beds, for they evidently contain a large amount of tuffaceous material and are often much coarser than the normal Binjura types. In addition, the differences are too pronounced to be explained as facies variations. This puts them into either the Coolringdon or the Bransby Beds, unless they constitute yet another series. The Coolringdon Beds on the one hand are almost entirely sedimentary in character, while the Bransby Beds contain a large amount of igneous material, tuff and limestone. No limestones or volcanic rocks are found here, and the beds are therefore placed temporarily with the Coolringdon Series.

Metamorphism.

Regional Metamorphism. The whole series has suffered a low grade of regional metamorphism and there is also a contact aureole along each of the igneous contacts. Thin sections show rocks varying from typical fine grained chlorite-sericite schists of low grade type to more siliceous and tuffaceous types with a matrix of chlorite, sericite and quartz. Thin section of a tuffaceous type shows irregular quartz, feldspar and rock fragments which on the whole are surprisingly little recrystallized. Many of the quartz grains indeed are barely changed.

Regional metamorphism in this area has thus produced rocks which are at highest in the chlorite zone. It is of interest to note, however, that the section of a rock on the Quidong Road in the Parish of Ashton revealed the presence of

biotite. No granite is known in this vicinity, although it may occur below the surface, and it is thus possible that the biotite was not formed by contact metamorphism. In addition, rocks along the Snowy River Road west of the Bukalong granite suggest a possible increase in metamorphic grade. As the place of the biotite zone in the metamorphic history at Cooma remains uncertain, examination of Ordovician rocks in this region may prove fruitful.

Contact Metamorphism. No true hornfelses have been formed in this area and original quartz fragments are often only partly recrystallized even at the igneous contact where red-brown biotite is developed in the matrix. The original schistosity becomes more prominent away from the contact but is always fairly well preserved. Spotted types appear in the outer parts of the contact aureole and seem to be restricted to the more pelitic types. A green mica occurs in place of the red-brown biotite away from the contact and is a prominent constituent of the spots. Distinct crystal outlines suggest that the spots were originally cordierite(?) but they now consist of the same minerals as the rest of the rock. No individual band can be traced through the varying stages of alteration and it is thus impossible to determine the exact changes which take place. The outer limit of the biotite seems to be almost coincident with that of the spotting so that this has been largely used as the criterion for determining the contact zone in the field.

(b) *Devonian.*

Rock Types.

The south-eastern part of the area is made up of sediments of Devonian age. A narrow strip carries northwards as far as the Reservoir and a small outlier also occurs beside the Bibbenluke Road west of the High Lake. Another outlier occurs near the village of Bibbenluke, ten miles north of Bombala, but mapping has not been extended as far north as this.

The beds, which are over 1,000 feet thick within the area examined, are made up of a variety of sedimentary types. The most common are grits—purple, red, grey or cream—while coarse massive conglomerates, sandstones and quartzites are also abundant. In addition to these a very characteristic rock is a red mudstone which occurs in intermittent bands throughout the series. The red beds are prominent in the basal parts of the series, where they form bands varying from only a few feet to 20 or 30 feet in thickness. At the Porphyry Quarry near the Hospital, for example, the basal Devonian beds are of red shale with an aggregate thickness of about 30 feet. These are overlain by 20 feet of conglomerates which are separated again from the thicker conglomerate capping (about 40 feet) by a further five feet of red shale.

The massive basal conglomerates which are well exposed amongst the interbedded sandstones, grits and mudstones above the Ordovician sediments on the Buckey Springs Road and again near the Reservoir turnoff on the Cathcart Road, appear to be rather more siliceous on the whole than those higher in the series and forming the hills further east. The sandstones and grits of the latter beds, however, are frequently very siliceous and may be more of the nature of quartzites. Whether or not this is related to any of the igneous activity which followed the Devonian era is difficult to decide. Similar quartzites have been described by Brown (1931) in corresponding beds on the coast further east, so that it seems to be some inherent feature of the sediments themselves. The distribution of the siliceous in contrast to the more normal sandstones appears to be purely fortuitous.

White mica is often developed along the bedding planes of the sandstones and the cementing material in most of the rocks is at least partly ferruginous.

Broadly speaking the series is divisible into three parts.

The lower stage has a thickness of about 150 feet and consists principally of massive siliceous and gritty conglomerates with interbedded red sandstones and mudstones. Purplish or reddish colours are common in the grits, while occasional buff-coloured types are also found. These beds of the lower stage form a rather prominent bluff facing the town, but fall away in a dip slope to the east. They swing eastwards near the Buckey Springs Road and front the COLUMBOOKA granite along its southern margin.

They are followed upward by a very much less resistant band which forms the cleared country along the Buckey Springs Road. Outcrops are often difficult to find except where a hard band forms a distinctive outcrop, but here the series appears to consist principally of red shales with a few conglomerates and some coarser sandstones, also of reddish colour. Behind the scarp formed by the basal beds, and the more prominent scarp of the upper conglomerates, this cleared area continues southwards, although of narrower width. Here, however, it is quite devoid of outcrop, but it is assumed that this too is part of the red shale horizon. The thickness of this stage is rather difficult to estimate, but it seems to be of the order of 200 feet.

The topmost stage here is the most prominent, forming a second and much higher scarp. South-east of the town this rises at first by relatively gradual increments, mainly over purple grits which are probably of tuffaceous character. With the appearance of bands of more resistant siliceous grits and sandstones, small vertical bluffs are formed, at first only about five feet high, but increasing in thickness towards the top so that they are often 20 feet or so high. They are separated by narrow bands of less resistance. The maximum thickness of these upper beds is 900 feet.

The total thickness of the series here is thus at least 1,200 feet. The conglomerates contain principally pebbles of quartz, quartzites and black slaty rocks evidently of Ordovician origin, in a gritty matrix. In many of the conglomerates, however, pebbles of Devonian rocks also occur, these being of gritty, sandy or shaly type and characterized by the red or purplish colour typical of the Devonian sediments. These are due either to brecciation under water of sandy or shaly bands forming contemporaneously, or else they are derived from earlier Devonian rocks exposed and consolidated.

Structure.

Two main difficulties have been encountered in the structural mapping of the Devonian strata; firstly the dying out of many of the beds, making it impossible to map one particular band for any distance; and secondly the frequent occurrence of current bedding, which may easily be mistaken for true bedding at the surface. In addition the outcrops beyond a mile or so from the western margin are scanty in distribution and are frequently quite unsuitable for strike and dip determinations.

The dominant strike of the beds seems to be between north-west and west-north-west, but strike directions dominantly east of north were found to hold across the central western part, and extend for nearly a mile to the highest scarp almost midway between the Roseneath and Buckey Springs Roads. This cannot be explained by simple folding since the general south-west dip still prevails further south, but it appears to be a warping across the general tilted structure. The presence of the porphyry disappearing below this seems significant but will be discussed in connection with the form of the latter intrusion. Slight folding is indicated by the surface outcrops near Roseneath. In general the beds are fairly gently dipping, the angle of dip being somewhat variable even in adjacent bands, from 10° to 30° . This variable character is probably due to current bedding.

Jointing is prominent in most of the rock types and the fine red mudstones are often shattered. Three prominent jointing directions sometimes give a sub-hexagonal pattern to the flat outcrops. Two principal directions are N. 70° W. and N. 10° W., with a third less perfect and rather variable jointing at about N. 50° E. The jointing is apparently independent of any warping since it seems fairly uniform throughout the series.

Relationship with Ordovician Rocks.

The unconformable junction between the Devonian and Ordovician strata is clearly seen at several points. On the Cathcart Road near the Reservoir, steeply-dipping Ordovician quartzites and slates forming a broad, pitching anticline are overlain by gently-dipping Devonian conglomerates and shales, the base of which is apparently irregular. Along the Buckey Springs Road gently-dipping sediments striking N. 15° E. overlie Ordovician strata whose strike is N. 10° W.

The differences in height of the junction in different parts of the area are noteworthy. This is seen most clearly near the Reservoir, where the base of the Devonian rocks against the Ordovician varies in height by 50 feet. The surface of deposition must have been highly irregular, since the feature appears to bear no relation to the Devonian structure.

Correlation.

No fossils have been found in any of these beds at Bombala, but their lithological similarity to some of the Upper Devonian rocks of the South Coast and elsewhere points to this as their probable—indeed almost certain—age. At Eden the Upper Devonian has been subdivided into three stages, and since no volcanic rocks occur within the present series, it appears to belong to the Upper or “Lambie” Stage. These beds at Eden “consist essentially of conglomerates, grits, quartzites and mudstones of shallow water origin” (Brown, 1931) which carry occasional marine fossils. They have a maximum thickness of 1,200 feet at Eden and this is also about the thickness developed at Bombala. The two series are lithologically very similar and the restriction of fossils at Eden to rare narrow bands may account for their apparent absence here. The evidences for correlation with the Lambie Stage are so strong that the Bombala Series can also be regarded as undoubtedly marine.

(c) Tertiary.

Distribution.

All rocks of Tertiary age are grouped together on the accompanying map (Plate V). The sediments and basalt are closely associated and thus “grey billy” is frequently found at the base of the basalt. Isolated patches of gravel are common, especially above the entrenched river, but are not indicated on the map. The boundary of the Tertiary sediments against the older rocks is frequently difficult to ascertain with accuracy, owing to lack of outcrops and the recent soil covering.

Of the Tertiary rocks marked, the northern area consists mainly of basalt with flat ridges of gravel and grey billy across the Coolumbooka Valley. This basalt stretches far to the north and is continuous with the widespread flows through Nimmitabel. In the southern area the basalt has been largely eroded, leaving extensive outcrops of resistant grey billy, with gravels covering most of the area. Above these, as near Lord’s Hill, ferruginous sediments are sometimes important.

Unconsolidated Sediments.

Patches of gravel, well above the height of the present river, are widely distributed through the area. They are very variable in character, some consisting of coarse rounded boulders of quartz, quartzite, etc., while others are of much finer texture and may be gritty or sandy. To the north of the Coolumbooka Bridge a gully has cut through at least 30 feet of bedded sandy grits, largely of granitic character. These must antedate the basalt in age, since, except for the topmost dark layer, no trace of basaltic material is revealed. Sometimes real granite gravels occur, almost identical with decomposed granite, as on the Bibbenluke Road past Bellview. A small area of horizontally-bedded sandstone, about 10 feet thick, caps the granite in the Coolumbooka Valley about three-quarters of a mile S.S.W. of the Coolumbooka Bridge. The maximum thickness of gravels measured was 100 feet where they are dissected by the Bombala River just within the Parish of Burnima.

Ferruginous Sediments.

Forming a ridge above the gravels near Lord's Hill is a capping of some 20 or 30 feet of horizontally-bedded ferruginous grits, sandstones and shales which contain numerous plant remains. They continue above the gravels towards Saucy Creek and form distinctive outcrops where dissected. They evidently post-dated the basalt quite considerably as they are immediately underlain by grey billy, and the high ferruginous character of the sediments is undoubtedly due to erosion of the vast covering of basalt over the land surface at that time.

They are possibly a lake deposit, and both in appearance and occurrence strongly resemble similar deposits near Cooma, Wingello, etc. "The Wingello fossil-bearing Tertiary beds", according to Jacquet (1901), "are found not only under sheets of basalt, but also over considerable areas without any protecting rock above them. They comprise beds of ferruginous shale, sandy claystones and coarse-grained sandstones." With reference to the lateritic iron ore at Wingello, Jacquet suggests that it "was formed in shallow lakes or rivers during late Tertiary times, essentially, but not entirely from basalt". These laterites have been described in a number of places in the eastern part of the State and it is noted that they nearly always overlie Tertiary beds. It is thus not unreasonable to suppose that the present highly ferruginous sediments are also the product of lake-deposition.

Grey Billy.

Silicification of the gravels in contact with the basalt has formed a resistant layer of "grey billy" which frequently remains after erosion of the igneous rock. The widespread occurrence of grey billy in this area is thus an indication of the former extent of the basalt. It occurs at heights varying from 10 feet above the river to 250 feet and usually forms low, flat outcrops. Where silicification has been more intense or erosion more rapid, the hard rock forms prominent outcrops up to 10 feet high and these may strongly resemble the tors formed by the quartz mica diorite.

In accordance with the sediments from which it is formed, the grey billy varies from fine grey, white or blue quartzites to coarse silicified conglomerates. Best outcrops occur on the Delegate Road beyond Saucy Creek, west of the Cann River Road about a mile past the Delegate turnoff, and in Macdonald's Creek north of the Cambalong Road.

On the Delegate Road opposite the Cambalong turnoff, a prominent white quartz hill stands above the level of the surrounding grey billy which is here packed with irregular fragments of quartz, and it seems that the basalt at one stage completely covered this hill.

The Basalts.

The basalts of this area are remnants of much more widespread flows undoubtedly continuous with those stretching north through Nimmitabel and Cooma. The maximum thickness attained here in 120 feet near the High Lake, and it seems apparent that the volume of lava extruded decreased towards the south.

The rocks are all basic in character, but are variable in grainsize and texturally may be porphyritic or non-porphyritic, holocrystalline or hypocrystalline, massive or vesicular. The essential constituents are a basic plagioclase (labradorite), titan augite, and iron ore (probably ilmenite). Olivine may be a major constituent, usually as phenocrysts, or may be entirely absent, while differences in the titania content of the pyroxene are also reflected in thin section. Zeolites are common in the interstices and may be associated with fine apatite needles, while further north near Nimmitabel where greater thicknesses of basalt occur, the rock is riddled with large amygdules filled with calcite and zeolites. Occasionally coarser segregation veins occur through the normal rock and in these the ilmenite is often in parallel plates.

Tertiary History.

Detailed examination of the relative heights of the Tertiary sediments above sea level, or of their relation to the present river system, has not been made but some observations are recorded here to indicate that valuable information about the Tertiary history might be obtained on detailed study.

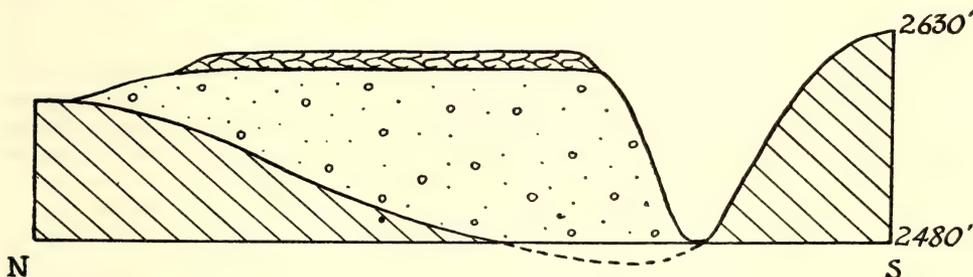


Fig. 1.—Section exposed by Bombala River at boundary of Parishes of Bombala and Burnima. The river has cut through the basalt capping, but has not yet reached the base of the Tertiary sediments. The floor of the Tertiary Valley was of slate. Scale, V : H = 1 : 3.

(1) Gravels are widespread and occur on top of the dissected Tertiary land surface up to 250 feet above the present river system. Gravels on which the town is built extend down almost to river level and rise as high as 200 feet above the river on the western side of the town. Near Burnima the river has cut through the capping of basalt and grey billy, but has not yet reached the base of the gravels, though dissection of 100 feet of gravels has been effected. (See Fig. 1.)

Saucy Creek has in places succeeded in cutting just below the base of the gravels which rise almost 100 feet above the stream.

“Granite Gravels” below the basalt (e.g. Por. 224, Parish Bombala) suggest the presence of small lakes in which the wash from the granite country was trapped.

(2) The basalt was evidently poured out over an uneven surface since great variations in its height occur. The accompanying readings are typical of the variable height of the base of the basalt. More than one flow has certainly

occurred, since bole (baked earth) has been found between flows in some parts, while springs and lakes are abundant. However, these probably represent only pulses in a single period of volcanic activity. No mineralogical characteristics have been identified with any particular flow.

Rock.	Height Above River in Feet.	River.	Locality.	Portion.	Parish.
(a) Grey Billy.	15	Bombala.	South of town.	301	Bombala.
(b) Grey Billy.	30	Bombala.	Macdonald's Ck.	37	Gecar.
(c) Basalt.	150	Bombala.	Near Burnima.	127	Bombala.
(d) Basalt.	250	Coolumbooka.	Near High Lake.	235	Bombala.

(3) The grey billy on Macdonald's Creek is surrounded by Tertiary sediments at much greater height. Moreover ferruginous sandstones, shales and grits overlie grey billy near Lord's Hill. They are therefore considerably younger than the basalt which had been eroded before their deposition. They thus appear to have been formed in a Tertiary lake, their ferruginous character being due to the basaltic nature of many of the rocks from which they were derived.

IV. INTRUSIVE ROCKS.

(a) *Plutonic.*

Three principal plutonic intrusions occur within this area. They are apparently of similar age and are thought to form part of a more extensive plutonic complex. Their general characters will be dealt with here, together with a brief account of their petrology. It is hoped to publish the results of more detailed petrological work later.

(i) **Bombala Intrusion.**

In the south-west of the area, and largely covered by Tertiary rocks, is a mass of quartz mica diorite about 15 square miles in area. It is intrusive mainly through Ordovician strata while on the eastern margin it is in contact with Devonian sediments. Except for marked variations in the height of the junction, however, their relationship is obscure, but the igneous rock is thought to intrude the sediments. It is cut off on the north by the later "Bukalong Intrusion" and a tongue of this also occurs within the eastern part of the mass. Two small outliers, one only 10 yards in length, are found at the eastern margin of the Bukalong intrusion in Portions 282 and 286, Parish Bombala, and are evidently remnants of a larger mass engulfed by the younger granite. Another mass, less than one-quarter square mile in area, intrudes the Ordovician rocks just east of here and has been called "Peadon's Intrusion". It also consists largely of quartz mica diorite which often appears to have suffered considerable contamination. At the southern end of the mass a fine biotite granite occurs and is undoubtedly related to the later Bukalong Intrusion but poor outcrops obscure the field relations.

The present terrain must be fairly close to the top of the intrusion. Small areas of Ordovician slate overlie it west of Paradise Hill, while at its junction with the Bukalong intrusion slate is found in several places.

The rocks are variable in character and appear to have been modified by contamination, especially towards the west. They are holocrystalline, with

medium or fine grainsize except for occasional large hornblendes which may attain a length of 1 cm. A slight directional structure is sometimes seen, marked principally by orientation of the hornblende crystals. Quartz is prominent among the macroscopic constituents, plagioclase (andesine) is abundant and a little irregular orthoclase may be seen. Biotite and hornblende are both present but their proportions, like those of the orthoclase and plagioclase, are variable. The fabric is hypidiomorphic granular, with subidiomorphic to idiomorphic plagioclase and hornblende. Biotite is in irregular plates and quartz and orthoclase are interstitial. Zircon, apatite and iron ore occur as accessories and a little green tourmaline is occasionally seen. Lenses of (?) prehnite are common separating the biotite cleavages.

The northern quartz mica diorite masses are undoubtedly related to the main Bombala Intrusion. Xenoliths are particularly abundant in these rocks and may attain dimensions up to two feet.

(ii) Coolumbooka Intrusion.

The typical rocks of this intrusion are granodioritic in character and fairly similar in appearance, but only the eastern tip of the mass has been examined and its full extent is unknown. A fine-grained biotite granite is also associated but will be described separately.

(a) *Granodiorite*. In general these rocks are medium-grained with some crystals attaining coarser dimensions. Visible constituents in hand-specimen are vitreous quartz, white or colourless plagioclase and pale pink orthoclase together with biotite and hornblende. The orthoclase is subordinate to plagioclase in amount and may show slight lustre mottling. The rocks are very similar in texture to those of the Bombala intrusion, but the proportions of the various minerals are different since the composition of the magma is more acid. Thus orthoclase is more abundant, plagioclase is rather more acid, and biotite is far in excess of hornblende. Apatite, zircon and iron ore are common accessories and a little interstitial calcite may be present. Several veins of tourmaline aplite have also been noted.

A porphyritic modification of the main intrusion occurs near the Parish of Coolumbooka, east of the Reservoir. Medium to coarse phenocrysts similar to the minerals of the normal rock are set in a fine-grained groundmass of more acid character, quartz and orthoclase being most abundant. Its relation to the main mass is, however, unknown since outcrops are sparse.

(b) *Biotite Granite*. A small mass of biotite granite, covering no more than an acre, outcrops near the Devonian boundary $1\frac{1}{2}$ miles north-west of the Bombala Trigonometrical Station. It is grey, medium-grained and massive with abundant, rather smoky quartz, and colourless felspar together with scattered flakes of biotite. Quartz, orthoclase, microcline and plagioclase (oligoclase) are dominant in thin section together with biotite and a little iron ore. The relation of this rock to the main granodiorite mass is not clear and although no distinct boundaries have been found between the two types, it probably represents a later intrusion, perhaps related to some of the Bukalong types. It is unfortunate that the Devonian rocks cover most of this mass.

(iii) Bukalong Intrusion.

This mass is of complex character, consisting of a number of different rock types whose field relations are by no means clear.

The southern tongue invading, and completely surrounded by the Bombala Intrusion is made up of porphyritic microgranites, aplites and coarse granites, the differences being largely textural and probably due to varying conditions of cooling, etc. These rocks weather rapidly so that fresh specimens are almost

impossible to obtain, and indeed this feature has proved a difficulty throughout most of the Bukalong mass.

The south-east part of the main intrusion is similar to this, but within the Parishes of Gecar and Pickering complex types are found. These have undoubtedly arisen by contamination but will not be discussed here. As yet it has been found impossible to separate the various rock types for field mapping.

The most normal rock appears to be a coarse biotite granite. Fresh specimens are obtainable only in railway cuttings where it is pink in colour. Normally the rock appears cream at the surface and is often stained with iron. Quartz, potash felspar and plagioclase (oligoclase) occur in comparable amounts, while biotite usually forms only a few per cent. of the rock. The potash felspar is largely of microperthitic character but microcline may also be present. Muscovite may occur as a primary mineral in some of these rocks but is often of secondary origin associated with irregular grains of fluorite. This, together with the presence of myrmekite (Sederholm, 1916), suggests that pneumatolytic processes have been active.

A fresher and somewhat finer rock is found near the Bukalong Road in the Parish of Pickering. It is fairly extensive but its relation to the coarser mass is indefinite and in thin section it is very similar to those rocks.

West of the Bukalong Road, and stretching into the Parish of Gecar, microgranitic types are found, rich in biotite and undoubtedly not of purely igneous origin. In Portions 288 and 292, Parish Bombala two small masses of fine-grained, biotite-rich granite show a definite boundary with the coarse granite which has cooled against them. They thus represent at least an earlier phase of the Bukalong injection, if not a separate intrusion largely engulfed by the younger mass.

Large dykes of aplite and quartz, forming prominent linear features such as those across Saucy Creek near the Racecourse, are probably a late phase of the Bukalong injection while "pipes" of quartz giving bare white hills appear to represent a still later phase in the activity.

(b) *Hypabyssal.*

The most important hypabyssal rocks in this area are porphyries and rhyolites, which are divided into two groups. The first comprises a single mass south of the town, while the second group includes numerous isolated dykes which find their maximum development at Paradise Hill. For convenience they have been termed respectively the "Hospital Porphyries" and the "Paradise Porphyries".

(i) **Hospital Porphyries.**

These rocks form a mass about one-quarter square mile in area, and rather elongated in plan. They cut mainly through Ordovician rocks but to the west they are in contact with the Bombala Intrusion. A small fault seems to have displaced them along the river. On the east they are covered by the high Devonian country, and the flat cleared paddocks devoid of outcrop at the foot of these hills are probably part of this intrusion and have been mapped with it. The rocks weather very rapidly and exposures are rare. A quarry has been cut into the series near the town (Portion 28), but even here the rock is by no means fresh, although a vertical prismatic jointing may be well developed. The top of the quarry is almost coincident with the base of the Devonian rocks, and just north of this stringers of porphyry are seen penetrating these sediments. The rock has been used for surfacing the local roads but the quarry is no longer worked.

A section along the river across this mass reveals a variety of rock types. At the northern boundary of the mass on either side of the river a greenish

coloured rock of brecciated appearance is dominant. Irregular unoriented fragments of Ordovician rocks, and sometimes of aplite, may occur as inclusions in these types. The rock itself is composed of a large number of oriented fragments which give it a pronounced flow structure. These are much drawn out and seem to have been either acquired at a stage when they were not wholly solid themselves or else rendered plastic during the injection. They are probably an earlier part of the same series of injections, brecciated by continued inflow of igneous material. Scattered phenocrysts of quartz and felspar occur in the fine, recrystallized groundmass while a little garnet and occasional flakes of dark mica may be seen. Flow structure is present in most of the rocks, but shows up particularly well in the marginal types and is undoubtedly due to the high viscosity of the magma at the time of injection.

A similar feature has been described in the Loch Bà Felsite Ring Dyke at Mull, where flow brecciation in a highly viscous magma is used to explain the breccia which sometimes occurs. The Mull dyke also consists of a "beautifully flow-banded rhyolite" (Hatch and Wells, 1937, p. 348), passing in places into a slightly more crystalline "felsite". It is 100 yards to one-quarter mile in width.

Away from the northern margin, inclusions become less abundant, the rock shows less perfect flow structure in hand-specimen, and phenocrysts are more prominent and regularly distributed, with garnet and biotite increasing in relative importance. The colour of the rock is very variable and this may be due to multiplicity of injection, but is also probably influenced considerably by the degree of weathering and of deuteritic activity. No sharp junctions have been found within the mass, and on the whole the rocks are very similar under the microscope, except in the proportions of phenocrysts and groundmass. However, fragments of contemporaneous material in the rocks at the northern margin show without doubt that the mass is not the product of a single injection.

Typical rocks of the main mass contain phenocrysts of quartz and orthoclase, together with some plagioclase and mica in a hypohaline or cryptocrystalline groundmass showing strong flow banding in thin section. The flow structure is emphasized by alternate bands of very finely crystalline and of coarser material. The latter seems to have formed by shrinkage and cracking along the flow directions with the formation of parallel fibres of orthoclase and quartz around the margin of the cracks. These project into a central area filled with pale green micaceous material in radiating masses or fibres. A little crystalline albite may also occur in these areas while the quartz and orthoclase frequently form a cryptographic intergrowth, and a sub-spherulitic character is common in the wider coarse bands. Phenocrysts are less abundant in these areas.

Evidence of deuteritic activity is abundant through these rocks and albitization may be intense. Fluorite is sometimes deposited in the felspar near quartz-albite veins which are very abundant through some of the rocks. Where these veins cut across the quartz phenocrysts, they are evidenced only by a trail of minute dark specks. High power shows that these are mostly minute liquid inclusions, frequently containing gaseous bubbles which can occasionally be seen to move in the liquid.

The exact form of this intrusion presents an interesting problem. It cuts more or less linearly across the strike of the Ordovician beds along its northern margin near the river and thus seems to be dyke-like in character. Near the quarry to the north-east, however, it penetrates only the very lowest Devonian sediments, in the form of small stringers and veins along the bedding planes.

The pronounced flow structure shows that the rock was in a highly viscous state during injection so that we may picture the magma welling slowly upwards in a dyke fissure through the Ordovician strata until these suddenly give place

to gently dipping Devonian sediments. The courses which the magma may then take are twofold. Either it may continue to pass upwards through these, or else it may be squeezed laterally along the unconformity which separates the two series. Actually both processes seem to have occurred here. The magma has partly exerted its declining strength in forcing narrow stringers into the Devonian rocks possibly along tension-cracks, but the main body of magma has taken the easier course and passed along the unconformity. The vertical prismatic jointing seen in the quarry walls confirms this view since jointing usually develops at right angles to the cooling surface. Moreover the cross-warping of the Devonian strata seems to strike more or less along the direction of the feeding dyke and is undoubtedly due to the forces accompanying the rising magma.

The structure is thus that of an interformational sheet, of restricted dimensions and probably rather laccolithic in shape, together with its feeding dyke striking approximately east-west. The present case is unusual in that the horizontal extent of the mass relative to the size of the dyke is hardly of the dimensions usual to such injected masses.

(ii) Paradise Porphyries.

In contrast to the Hospital Porphyries, the rocks of the Paradise dykes are usually less decomposed and show considerably more variety of grain size and texture, etc., as well as being scattered in their distribution. They are found penetrating the slates near the margin of the plutonic masses in the south and west of the area but most are confined within the Bombala and Bukalong intrusions. They find their maximum development at the junction of these intrusions at Paradise Hill, where they unite into a large mass standing above the general land surface. This mass alone has been drawn on the accompanying map since individual dykes, usually only of relatively narrow width, are too numerous to be plotted on this scale. Dykes continue in abundance across the river west of here and are mostly sub-parallel. This feature appears to hold for most of the series but some cross-cutting dykes are also found.

The dykes are simple or multiple and vary in width from three or four feet to 20 yards, except for the Paradise Hill mass itself, which is really a multiple dyke with a width of nearly half a mile. The strike directions of some 50 dykes have been measured, but dips usually cannot be determined. Sometimes beautiful prismatic jointing is developed across the dykes and this is particularly well seen in horizontal pavements on the western slope of Paradise Hill. The strike of the majority of the dykes lies within the limits N. 30° W. to N. 15° E. and detailed examination of the dyke system would doubtless prove fruitful. Individual dykes are difficult to trace throughout their whole length but may be as long as a mile or more.

They thus seem to constitute a "dyke swarm", but no other record of acid rocks with this structure has been found.

The series is entirely of acid character with rocks varying from non-porphyrific types showing beautiful flow structure in hand-specimen, to porphyries in which the felspar phenocrysts may be one inch or more in length. In the multiple dykes both porphyritic and non-porphyrific types may occur, the latter usually representing the first injection and reflecting a strong flow-banding.

Phenocrysts are common in most of the rocks but vary both in size and amount. Quartz and felspar are most abundant, while small well formed garnets up to one-quarter inch in diameter and similar in colour to those of the Hospital Porphyries may also occur. A little ferromagnesian material is sometimes seen in hand-specimen. Occasional inclusions, both accidental and cognate, may be present. The felspars consist of both orthoclase and acid plagioclase, the former being usually in greater abundance, but the relative proportions of

the different phenocrysts are variable throughout the series. The phenocrysts, and especially those of quartz, may be idiomorphic, but are frequently broken up and the various stages from single idiomorphic crystals to scattered rounded fragments can often be traced. (Fig. 2.)

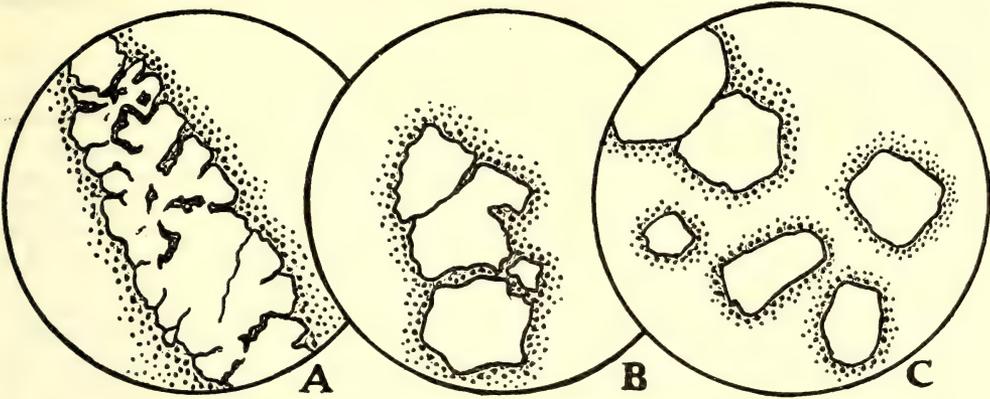


Fig. 2.—Diagram illustrating the progressive disintegration of idiomorphic quartz phenocrysts as result of attack by groundmass; and consequent presence of rounded fragments through the rock. Drawings from thin sections of Paradise Porphyries.

The orthoclase may show some albitization and the surface of the crystals is often clouded in thin section, while the plagioclase is albitic in composition. Biotite may occur with the phenocrysts but is often very altered, as in the Hospital Porphyries. Hornblende may have been present originally in a few of the rocks but is now completely altered. Occasional apatite and zircon crystals may be scattered through the rocks.

The groundmass is usually cryptocrystalline to microcrystalline with cryptographic fabric developed to varying degrees. It may be very similar to some of the Hospital Porphyries but is often coarser than these. A characteristic

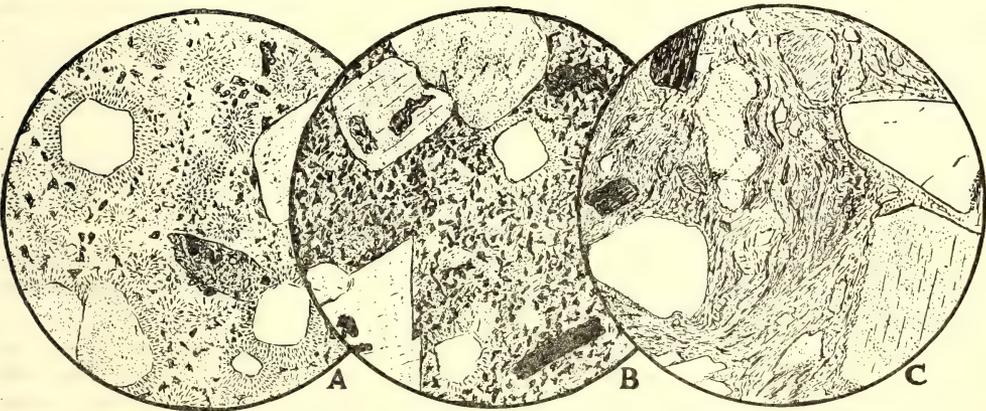


Fig. 3.—Thin sections of Paradise Porphyries illustrating different types of groundmass. A. Groundmass largely spherulitic. B. Ferromagnesian material abundant in groundmass except around quartz grains which show "reaction rim" of cryptographic quartz and felspar. C. Flow banding strongly developed by hypohyaline to cryptocrystalline groundmass.

feature is the development of a cryptographic rim devoid of dark minerals around the phenocrysts, especially around the quartz (see Fig. 3B). This is probably due to acidification of the magma immediately surrounding the grains during their disintegration, and is thus a type of reaction rim around the phenocrysts. Sometimes the groundmass acquires a sub-spherulitic character, the dark minerals being confined to the spaces between these, and the spherulites arranged along the flow direction.

(iii) Basic Dykes.

Several small basic dykes have been found and are probably related to the Tertiary volcanic activity. One of these, occurring east of Paradise Hill in Portion 32, Parish Bombala, shows phenocrysts of vitreous green olivine, and rare small black pyroxenes in a basaltic groundmass composed of tiny well formed laths of plagioclase together with irregular granules of iron ore. Occasional small white ovoid patches of zeolitic material may occur and these are lined by a zone of small projecting crystals of pyroxene. A dyke of similar rock in Portion 95, Parish Gecar, is particularly rich in pyrites. A very weathered dyke through the Ordovician slates is revealed in the railway cutting in Portion 113, Parish Bombala. It was probably also originally of basic character but now shows only a strong spheroidal weathering. This suggests that more of these basic dykes probably exist through the area but are too weathered to appear at the surface.

(c) *History of Intrusion.*

The interpretation of the intrusive history of the present igneous rocks presents some difficulties. The Bombala and Bukalong Intrusions appear to be stocks forming part of a composite bathylith. The eastern granite seems, from petrological considerations, to be part of the same plutonic complex and might be connected underground with the western mass. The abundance of xenoliths in this rock, and more especially in the Bombala Intrusion, would in the opinion of many workers indicate a proximity to the roof of the intrusion. It is evident that the successive magma injections each succeeded in enlarging the size of the bathylithic mass and did not simply enter successively into the same chamber.

Mode of Intrusion. That stoping played an important role in the emplacement of the plutonic rocks is certain, and while folding of the country rock may have accompanied the initial magma injection it seems to have been only of minor importance. Many suggestive aspects of the problems of stoping have been compiled by the Committee on Bathylith Problems under the title "Comments on Magmatic Stopping" (1935). In addition to the abundance of xenoliths, particularly in the more basic types, and the transgressive form of the intrusions, a number of observations here accord with their findings and are worthy of note.

(i) In many creek sections, tongues of acid granite are seen penetrating the Ordovician slates and in places the latter are intimately penetrated by stringers of quartz and aplite from the granite.

(ii) "Re-entrant and step-like" junctions (cf. Barrell, 1907) are seen on the south bank of the Bombala River near the Racecourse, where fine-grained offshoots of the acid Bukalong granite are seen to penetrate the Bombala mass along joint planes and represent the first stage in the rifting away of blocks of country rock.

(iii) On a larger scale parallel aplitic dykes east of Paradise Hill have penetrated along joint planes in the quartz mica diorite.

(iv) The small quartz mica diorite outliers at the eastern margin of the Bukalong granite give similar evidence of stoping. The smaller one is entirely surrounded at the surface by an aplitic phase of the acid granite and had injection proceeded for a short time longer the block, which is only about 10 yards long and a few yards wide, would have been entirely stoped away. The northern block is similarly penetrated and largely surrounded by the acid granite.

(v) The isolated block of quartz mica diorite in the southern tongue of Bukalong granite east of the Racecourse is also suggestive of stoping and may represent either a block stoped away late in the intrusive process, or else a roof pendant.

Intrusive History. The quartz mica diorite seems to have been the first of the series of injections forming the present complex, although some of the xenoliths within it suggest that it may have been preceded by a more basic magma now completely displaced. That the Bukalong Intrusion occurred after this is certain, but the position of the Coolumbooka Intrusion in the sequence is unknown as it is nowhere in contact with the other types. The general sequence of events suggests decreasing basicity as a factor in the order of intrusion and it is thus suggested that the Coolumbooka granodiorite followed the quartz mica diorite in its injection. This is corroborated by the apparent genetic relationship of the Coolumbooka rocks to the rest of the series and the usual order of intrusion in complexes of this type. The biotite granite associated with it may belong to the same stage as some of the early members of the Bukalong complex. The latter injection probably extended over a considerable period, giving rise to a number of different rock types which occasionally show an intrusive relationship to one another. The magma was, however, frequently modified by contamination with the country rocks. The aplites were probably in part contemporaneous with the acid injections, representing the initial stages of injection along joints, etc.

The dying stages of the diastrophism were evidently marked by the more or less simultaneous injection of the Hospital Porphyries and Paradise complex, although the relation of the former to the intrusive series is not certain. The final stages were marked by dykes of quartz and aplite such as those across the Racecourse and on Saucy Creek, and by great masses of quartz forming dykes or pipes either within the granite near its margin, or penetrating the country rocks, when the granite can safely be assumed to lie fairly close below the land-surface.

Age. The age of the intrusion is not definite. Small aplite offshoots penetrate the Devonian sediments in the southern part of the Coolumbooka granite, and a consideration of the contour of the base of the Devonian rocks, which varies considerably within a few hundred yards near the Reservoir, also suggests an intrusive relationship between them, although the Ordovician-Devonian boundary nearby is also quite irregular. The general lack of metamorphism in the Devonian rocks is another factor which has not yet found satisfactory explanation. A few sediments carrying biotite occur near the aplite offshoots in Portion 93, but this mineral seems to be definitely of primary origin and is probably due to the tuffaceous character of the rock. Thin section shows that even the shale fragments in these rocks have not developed biotite, and while a few show a little recrystallization, many are unaffected. On the other hand contact effects in the Ordovician slates have never reached a high metamorphic grade either. It may be significant that some bands in the series are highly siliceous but unless some obscure agency has enabled the transfer of heat through to these highly siliceous bands—a highly improbable and unsatisfactory explanation—the problem must be left open and the Coolumbooka Series assumed to be younger than the Devonian sediments.

The relation of the Hospital Porphyries to the Paradise Intrusions is also important in determining their age. The character of the rocks is so similar, however, that there seems little doubt of their consanguinity, the Hospital types having suffered more deuteric activity, possibly because they were intruded more or less simultaneously and are not isolated.

The junction between the Hospital Porphyries and the quartz mica diorite near the river is unfortunately covered by soil and gravel, but occasional inclusions of aplite in the Porphyries suggest that they were intruded after the plutonic rocks were emplaced. If their consanguinity with the Paradise Porphyries is assumed then it is evident that the Hospital Porphyries post-date the quartz mica diorite. They are definitely intrusive into the Devonian sediments and hence the western intrusive rocks at least are post-Devonian. If the Coolumbooka Intrusion be interpolated into its natural place in the series, it is then also post-Devonian, and the series is assumed to belong to the diastrophism which terminated the Devonian period and termed by Sussmilch (1914) the Kanimbla epoch. This is the age ascribed to these rocks in a general way by Browne (1929, p. 24).

V. PHYSIOGRAPHY.

The mature topography between Nimmitabel and the Victorian border beyond Delegate has been considerably influenced by the nature of the country rocks. This, together with the extensive occurrence of basalt and of Tertiary sediments, gives to the area a rare topographic interest. A brief outline of some aspects of the physiography of the district will be given here.

(a) *Topography.*

The town of Bombala, with a height of 2,313 feet above sea level, lies in the southern part of what Sussmilch (1909) termed the Yass-Canberra or Monaro peneplain. Some ten miles to the east this plain descends steeply down the Coastal Range to the Coastal Plain, which has a width here of about 30 miles. The descent is of the order of 2,000 feet and is for the most part inaccessible. To the west the mature countryside carries for some distance till it gives place to the high mountains known as the Southern Alps. These include Mt. Kosciusko (over 7,300 feet), the highest point in Australia, at a distance of 65 miles direct from Bombala, and during the prolonged winter months the snow-capped Alpine ridges can be seen from many of the Bombala hilltops.

The eastern part of the area shows well the structural influence of the Devonian rocks in its evolution. Gently inclined dip-slopes are thus a common sight against the eastern skyline. The jointing in these rocks has also caused the development of cliff-like scarps at the western margin of the more massive strata. The red shales on the other hand have weathered much more readily and tend to form smooth, depressed areas among the more resistant grits.

The relief of the eastern zone is greater than that of the surrounding plain, the height rising to 3,144 feet at the Bombala Trigonometrical Station. Across the town to the west the relief is not so marked, the highest point being at "Paradise Hill", some 400 feet above the river and about 2,700 feet above sea level. This feature is due entirely to the resistant character of the rhyolites and porphyries of which it is composed relative to the surrounding granites. The "Hospital Porphyries" near the town, by contrast, have weathered more readily and do not rise above the general level of the surrounding slates.

The granite country, like that of the slates, has an undulating contour except where dissection by the river has caused the development of steep valley walls in the slate country. In the nature of their outcrops, however, as well as in their vegetation the principal plutonic rock-types are readily separable in the field. The coarse Bukalong granite weathers rapidly forming low flat outcrops

with little soil covering so that as a rule this country is rather poor. The finer "Bukalong" types are more resistant and may form prominent rugged outcrops. The rocks of the "Bombala" intrusion, on the other hand, weather less rapidly and form the characteristic rounded tors at the surface. The soil thus formed is also richer, possibly because of its higher iron content, and bears more profuse vegetation. This difference is also reflected in the fact that the areas of more basic rock have generally been cleared earlier than the acid types, which in places are still uncleared. The eastern granite from which the Coolumbooka River has carved its valley forms low, cleared undulating hills capped on the west by flat-topped basalt scarps and on the south by the rough Devonian hills.

Extensive Tertiary sediments across the southern part of the area form a flat-topped unit into which the streams are now cutting with considerable effect.

(b) *The Drainage System.*

The whole of the Monaro peneplain south of the main "Monaro" Divide which passes through Nimmitabel in a north-westerly direction, forms part of the drainage system of the Snowy River.

The Bombala River has its headwaters near the Brown Mountain and flows southward in a meandering course through Bibbenluke, being joined by the Coolumbooka River below the Bombala Reservoir. It meanders south through the Parish of Bombala to below the town, where it swings back in a north-westerly direction and follows a fairly straight course till it is joined by Brugolong Creek, where it again changes direction towards the south-west and joins the Delegate River near Quidong.

Some indication of the circuitous course taken by the river can be gleaned when it is realized that in a direct southerly distance of four miles from where the river enters from the Parish of Burnima to where it swings westward below the town, the present river course covers some eleven miles. The average gradient throughout this stretch is about 15 feet per mile.

The dissection of the land surface is, however, much greater than would be expected in a stream of such mature character, and this may be taken as evidence of its rejuvenation. The maximum dissection is usually about 150 feet. The amount of water which the streams carry varies considerably with the season. After heavy rains upstream the Bombala River often rises 30 feet, while even in the driest season it is never empty because of the large number of springs in the basaltic country to the north.

VI. SUMMARY.

A plutonic complex of Kanimbla age is intrusive through Upper Ordovician slates and Upper Devonian red-beds of Lambie Type. Three main intrusions occur, consisting of quartz mica diorite, granodiorite and biotite granite respectively. Contamination has modified some of these but is not discussed in detail here. Associated with these plutonic rocks is a very interesting dyke swarm of highly acid character and frequently carrying garnet. Tertiary sediments and basalt cover much of the area and give promise of useful results on detailed study.

VII. ACKNOWLEDGEMENTS.

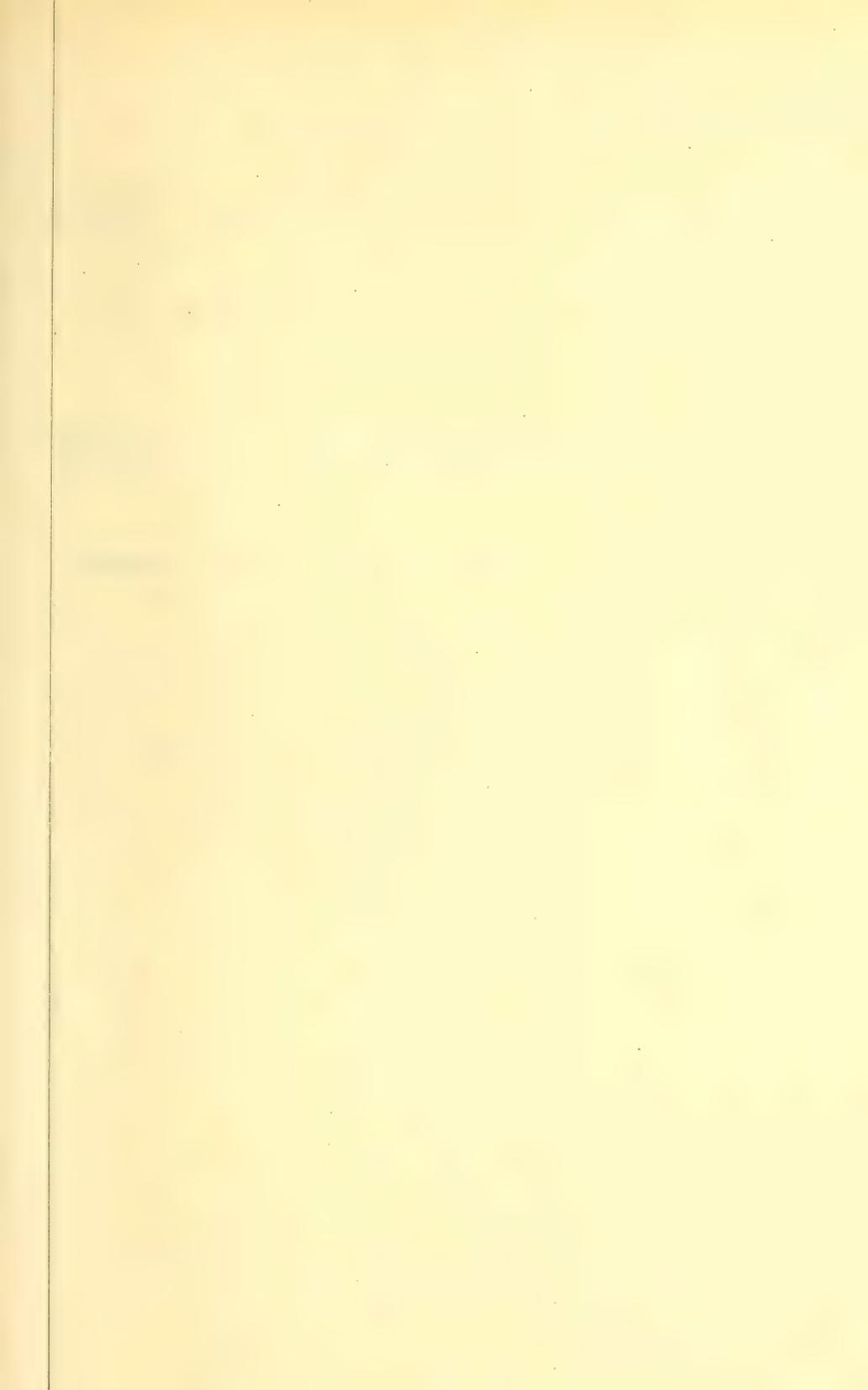
The sincere thanks of the writer are due to all those who helped her in this work; in particular to Dr. G. A. Joplin and Dr. W. R. Browne and others associated with the Department of Geology in Sydney University, where all laboratory work has been carried out; to Dr. A. H. Voisey of New England University College; and to Mr. and Mrs. J. P. Baillie, Mr. and Mrs. David

Garnock and other residents of Bombala for hospitality and kindness during field work.

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VIII. REFERENCES.

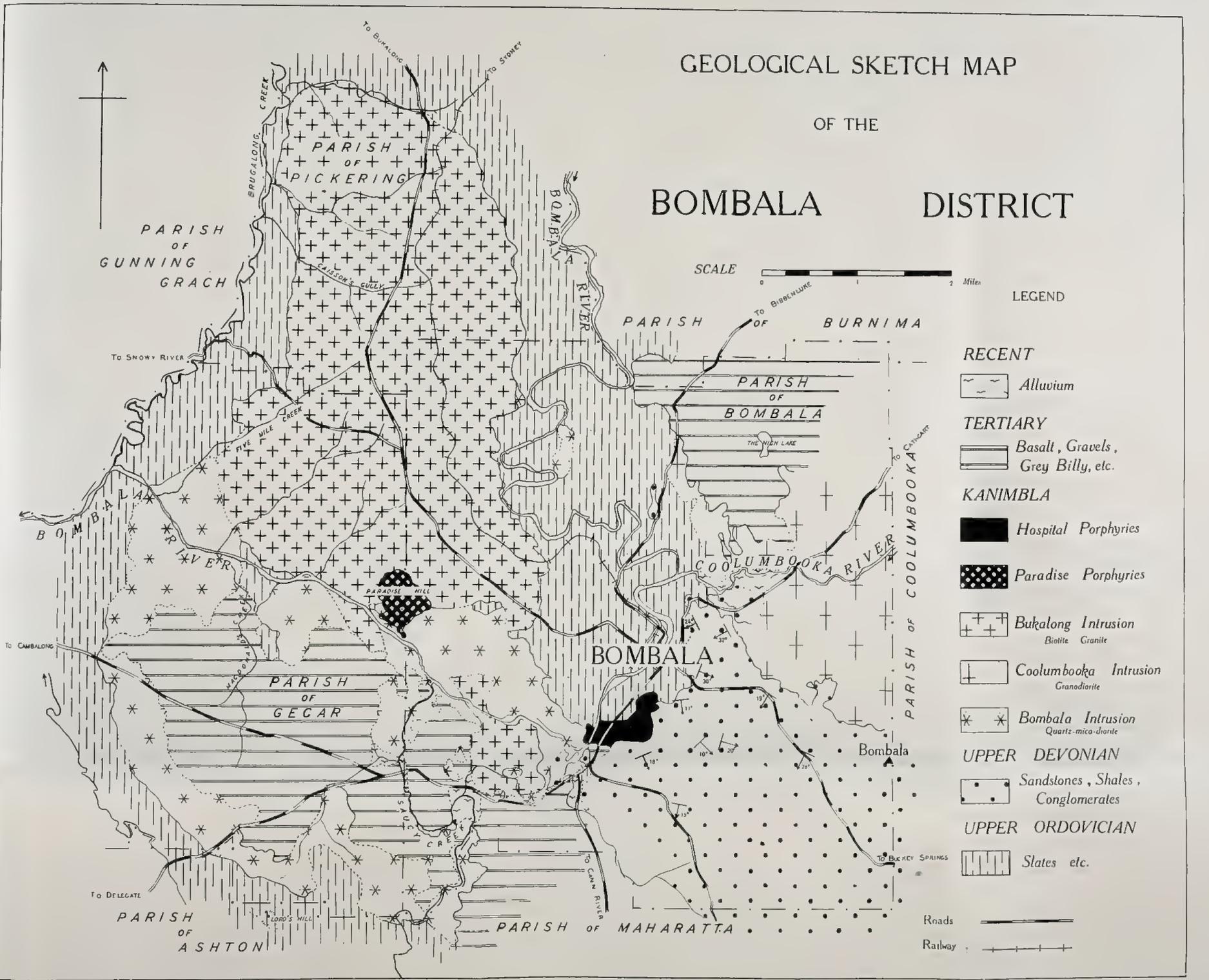
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GEOLOGICAL SKETCH MAP

OF THE

BOMBALA DISTRICT



SCALE 0 2 Miles

LEGEND

RECENT

Alluvium

TERTIARY

Basalt, Gravels, Grey Billy, etc.

KANIMBLA

Hospital Porphyries
 Paradise Porphyries

Bukalong Intrusion
 Biotite Granite

Coolumbooka Intrusion
 Granodiorite

Bombala Intrusion
 Quartz-mica-diorite

UPPER DEVONIAN
 Sandstones, Shales, Conglomerates

UPPER ORDOVICIAN
 Slates etc.

Roads
 Railway

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART X. THE OXIDATION OF CÆSIUM HEXACHLORO-RHODATE III TO CÆSIUM HEXACHLORO-RHODATE IV.

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Manuscript received, November 6, 1947. Read, December 3, 1947.

It is well known that in most of its compounds rhodium is trivalent, but as the centre member of the triad containing cobalt and iridium it might also be expected to display the bivalency and tetravalency characteristic of these elements. The existence of simple rhodium II salts is doubtful (Dwyer and Nyholm, 1941), despite the preparation of deeply coloured impure salts by the authors, and recent experiments indicate that the simple ion Rh^{++} undergoes disproportionation to trivalent rhodium and the free metal. A number of complex salts of rhodium II have been prepared, however (Dwyer and Nyholm, 1941, 1942, 1943).

The only compound of tetravalent rhodium described in the literature is the green hydrated dioxide $\text{RhO}_2 \cdot x\text{H}_2\text{O}$, originally obtained by the chlorination of sodium rhodate III, when it appeared as a precipitate, leaving a violet blue solution, which was claimed to contain hexavalent rhodium as sodium rhodate VI, Na_2RhO_4 (Claus, 1860). Wohler and Ewald (1931) showed that the oxide prepared by Claus had an oxygen content between Rh_2O_3 and RhO_2 and succeeded in preparing the dark green hydrated oxide in purer form by the anodic oxidation of sodium rhodate III. It was noted that the oxide dissolved in hydrochloric acid with the liberation of chlorine and the formation of the usual red rhodium III chloride, but the evidence did not distinguish unequivocally between a true quadrivalent oxide and a peroxide. Ruff and Ascher (1929), by the fluorination of rhodium sponge, obtained RhF_3 , as well as small amounts of a red-brown sublimate with a higher fluorine content but were unable to decide whether the substance was a tetrafluoride or a pentafluoride. Grube and Gu (1937) made an extensive study of the anodic oxidation of rhodium III salts in sulphuric, nitric and perchloric acids and found that the oxidation yielded first a green solution, which finally became violet. From potentiometric titrations of the oxidized solutions it was concluded that the green solutions contained quadrivalent rhodium and the violet hexavalent rhodium, present probably as the acid H_2RhO_4 . Evidence was adduced to show that the quadrivalent compound underwent disproportionation: $3\text{Rh}^{\text{IV}} \longrightarrow \text{Rh}^{\text{VI}} + 2\text{Rh}^{\text{III}}$. The redox potential of the quadrivalent/trivalent system was found to be approximately 1.40 volts. Studies of this system now being carried out indicate that this potential is actually somewhat higher. Grube and Auteriet (1938) failed to oxidize chloropentammine rhodium III perchlorate, potassium hexacyanorhodate III, or rhodium trifluoride in hydrofluoric acid. In the latter oxidation a green precipitate of (probably) the hydrated oxide was obtained at the anode.

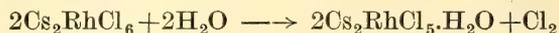
The most characteristic and stable compounds of most metals in the quadrivalent state are the alkali metal hexahalogenates R_2MX_6 , which form an

isomorphous series crystallizing in the cubic system, and the isolation of a complex of this type, it was felt would provide the best evidence for the existence of quadrivalent rhodium. Since the chloro compounds are the best defined of these complexes, the preparation of the compounds R_2RhCl_6 has been attempted.

Although the potential of the Rh^{IV}/Rh^{III} system is above the potential of the chlorine/chloride electrode, it can be deduced from the ordinary redox equation that if the concentration of quadrivalent rhodium is kept sufficiently low by the formation of an insoluble complex that trivalent rhodium can be oxidized by chlorine, i.e. in the presence of chloride ions. Among the platinum metals the solubility of the chloro complexes decrease notably as the size of the cation R is increased, and normally the caesium compound is highly insoluble.

In the initial series of experiments cold solutions of rhodium trichloride in the presence of caesium chloride were treated with chlorine or oxidized anodically. Traces of a green insoluble material with pronounced oxidizing properties were isolated, but the yields were extremely low, and the product was contaminated with a reddish non-oxidizing material. The amount of the green substance could be increased by the addition of hydrochloric acid and boiling just prior to the oxidation. Rhodium trichloride is well known to yield three types of complex with alkali halides: R_3RhCl_6 ; $R_2RhCl_5 \cdot H_2O$ and $RRhCl_4 \cdot 2H_2O$, and in solution in the presence of chloride ions there appears to be an equilibrium between the ions $RhCl_6'''$, $RhCl_5 \cdot H_2O''$ and $RhCl_4 \cdot 2H_2O'$. The beneficial effect of hydrochloric acid is thus due probably to the movement of the equilibrium to favour the ion $RhCl_6'''$ which appears to be the ion capable of oxidation. However, it was found that a large excess of chloride ion or hydrochloric acid completely inhibited the formation of the green substance. The oxidizing potential of chlorine falls with increasing chloride ion concentration, and apparently, in the presence of sufficient chloride ion to stabilize the $RhCl_6'''$ ion, the available potential is too low to permit oxidation.

The difficulty was finally overcome by isolating the $RhCl_6'''$ ion as the caesium salt Cs_3RhCl_6 in the form of a very fine precipitate, suspending it in ice water in the presence of a little caesium chloride and immediately oxidizing with ceric nitrate, when it was transformed quantitatively to the very sparingly soluble, green, compound caesium hexachlororhodate IV, Cs_2RhCl_6 . The compound decomposed rapidly in the presence of water with the liberation of chlorine and the formation of the reddish crystalline caesium aquo pentachloro rhodate III, $Cs_2RhCl_5 \cdot H_2O$.



It was instantly reduced with a colour change to rose red by bromide ions, sulphurous acid, ferrous sulphate or stannous chloride. Owing to the rapid decomposition in the presence of water it was not possible to dry the substance sufficiently rapidly to obtain samples for analysis, and the analysis was carried out on the wet material and the composition deduced from the ratio of the constituents.

The constitution was confirmed by X-ray powder photographs on very small samples dried rapidly in vacuum over phosphorus pentoxide. The perfectly dry material is stable. The substance was face centred cubic, isomorphous with ammonium chloroplatinate. The length of the side of the unit cube $10 \cdot 2 \text{ \AA}$. is very close to value for caesium hexachloroplatinate. From the structure parameter, $u = 0 \cdot 23 \pm 0 \cdot 01$, the distance $Rh^{IV}-Cl$ is $2 \cdot 3 \text{ \AA}$.

Attempts to oxidize potassium, ammonium or rubidium hexachlororhodate III were unsuccessful.

EXPERIMENTAL.

Cæsium Hexachloro-Rhodate IV. Anhydrous sodium hexachlororhodate III, prepared by fusion of rhodium black with sodium chloride in chlorine (0.5 g.), was dissolved in water (7 ml.), cooled to 0° and rapidly brought into solution. Traces of rhodium metal were removed by centrifuging in a tube cooled in ice. (If the sodium salt is allowed to stand or become warm, it is rapidly transformed to the aquo-pentachloro compound.) Cæsium chloride (1.0 g.) was added immediately, and the mixture shaken, when a pale rose-coloured precipitate of the cæsium compound resulted. The precipitate was centrifuged to the bottom of the tube and the supernatant liquid removed. A further 0.2 g. of cæsium chloride was added to the precipitate, followed by 12.5 ml. of ice cold ceric nitrate (0.1 N.) in nitric acid (1.1 N.) saturated with chlorine. On shaking, the mixture became a deep bluish green. This precipitate was centrifuged, the mother liquor removed, and fresh ice cold ceric nitrate added. This was repeated again, and the precipitate washed twice with ice cold nitric acid 0.1 N. Thin smears of the green compound were rapidly dried in vacuum over phosphorus pentoxide for the X ray examination, and the remainder of the material immediately used for the analysis.

The oxidation of cæsium hexachlororhodate III could be effected with potassium permanganate provided nitric acid stronger than 3 N. was mixed with it, but potassium dichromate was ineffective.

Analysis of Cæsium Hexachloro-Rhodate.

(1) *Ratio of Total Chlorine to Oxidizing Chlorine.* The material in the centrifuge tube was immediately treated with an excess of approximately 0.1 N. ferrous sulphate, and the excess determined by potentiometric titration with *sodium permanganate*. At the end of the titration a few drops of ferrous sulphate were added to prevent loss of the chlorine by reaction with the permanganate. The solution was then made up to 100 c.c., and 25 c.c. were treated with excess of 0.05 N. silver nitrate and a little concentrated nitric acid. The mixture was heated to precipitate the silver chloride completely, then diluted with water, and the excess silver nitrate determined with standard thiocyanate with ferric alum as an indicator.

Found: Total chlorine = 0.01575 g.; oxidizing chlorine = 0.00244 g. The ratio is thus 6.4/1.

(Although this is higher than the theoretical value 6.0/1, it should be noted that the ratio is increased by traces of chlorine not washed out during the preparation as well as direct loss of chlorine from the oxidized substance.)

(2) *Ratio of Rhodium to Total Chlorine.* A portion of the solution reduced with ferrous sulphate was treated with pure zinc dust and boiled to precipitate rhodium metal. After treatment with sulphuric acid, the metal was weighed.

Found: Rh = 0.0078 g.; Cl = 0.01575 g. Rh/Cl = 1/5.9. Calculated Rh/Cl = 1/6.

(3) *Ratio of Cæsium to Chlorine.* A portion of the solution reduced with ferrous sulphate was heated to boiling and made alkaline with sodium hydroxide. Drops of hydrogen peroxide were then added to complete the precipitation of ferric, rhodium and manganese hydroxides, and the precipitate removed. The filtrate was concentrated and the cæsium precipitated with chloroplatinic acid in the presence of alcohol.

Found: Cs₂PtCl₆ = 0.0494 g. or 0.0195 g. Cs; Cl = 0.01575 g. Cl/Cs = 3.02/1. Calculated: Cl/Cs = 3.0/1.

The Decomposition of Cæsium Hexachloro-Rhodate IV in Water.

Some of the green material was allowed to stand in contact with distilled water for two days. Chlorine was evolved and the material passed partly into solution and part gave brownish red prisms. The red solution on evaporation also gave reddish brown prisms. Analysis for chlorine and rhodium showed the substance to be cæsium aquo-pentachloro-rhodate III.

Found: Cl = 31.7%, 31.4%; Rh = 18.3%. Calculated for Cs₂RhCl₅.H₂O: Cl = 31.47%; Rh = 18.24%.

The Crystal Structure of Cæsium Hexachloro-Rhodate IV.

X-ray diffraction photographs of the following powder specimens were taken: (I) The starting material, cæsium hexachloro rhodate III, $\text{Cs}_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$; (II) the green powder, cæsium hexachloro rhodate IV, Cs_2RhCl_6 ; (III) the decomposition product, cæsium aquo pentachloro rhodate III. Photographs were taken in a 9 cm. camera and specimens I and II in a 19 cm. camera. With specimens I and III the material was placed on a glass fibre, but II was packed into thin celluloid tubes and sealed. Exposure times with filtered Cu radiation from a G.E. diffraction tube were 1 hr. in the 9 cm. camera and 4 hrs. in the 19 cm. camera. The green material did not appear to decompose during the exposures.

TABLE I.

Calculated and Observed Intensities of Reflections for Values of u between 0.20 and 0.25 Å. for Cs_2RhCl_6 ; Space Group O_h^5 ($Fm\bar{3}m$); $a=10.2 \text{ \AA}$.

Line N.*	Calculated Intensities. $u =$						Observed Intensities. Film		
	0.25	0.24	0.23	0.22	0.21	0.20	1	2	3
3	5.2	6.1	7.0	7.6	8.2	8.8	5	5	5
4	2.6	2.6	2.5	2.4	2.3	2.1	—	—	v.w.
8	9.6	9.6	9.7	9.9	10.1	10.5	10	10	10
11	4.0	3.8	3.7	3.5	3.5	3.6	—	2	2 to 3
12	7.7	7.6	7.5	7.4	7.1	6.9	8	8	8
16	8.4	8.4	8.2	8.1	7.9	7.6	9	9	9
19	2.8	2.1	1.6	1.1	0.7	0.4	—	—	1
20	1.5	1.6	1.8	1.9	2.1	2.3	—	—	1
24	6.2	6.2	6.1	6.0	5.9	5.8	6	6	7
27	2.3	2.9	3.3	3.7	4.1	4.3	2	2	3
32	6.8	6.7	6.6	6.3	6.0	5.8	7	7	7.5
35	2.3	2.6	2.8	3.0	3.1	2.0	2	—	3
36	1.5	1.7	1.8	2.0	2.3	2.65	—	—	1
40	4.3	4.4	4.6	4.9	5.3	5.7	4	4	4
43	0	0	0.2	0.5	0.8	0.9	—	—	—
44	4.1	4.0	3.8	3.4	3.0	2.6	3.5	< 3.5	4
48	3.9	3.9	3.7	3.5	3.2	3.0	3.5	> 3.5	4
51	1.7	2.0	2.5	2.7	2.9	3.1	1	—	2.5
52	0.75	0.7	0.7	0.6	0.5	0.4	—	—	< 1
56	4.4	4.4	4.6	4.9	5.0	5.3	5	5	5

$$* N = h^2 + k^2 + l^2.$$

Specimen I gave a diffraction pattern which was not cubic; II gave a simple pattern with reflections agreeing with a face centred cubic lattice; III gave a complex diffraction pattern. On some of the photographs of II one or two reflections appeared which were additional to those expected from the cubic system, but these lines always coincided with the most intense lines of the decomposition product. From the diffraction data a value of the lattice parameter a was found to be 10.2 Å. This constant could not be determined more accurately owing to the difficulty of indexing the high angle lines.

An examination of the indices of the reflections present indicated that the space group O_h^5 ($Fm\bar{3}m$) was a possible one and that the substance could therefore be isomorphous with ammonium chloroplatinate. Density determinations could not be made on the material, but if the assumption of isomorphism is correct there would be four molecules per unit cell. With these assumptions and taking $a=10.2 \text{ \AA}$, the expected intensities of reflections of the powder reflection lines were calculated for a structure parameter u lying between 0.17 and 0.25. These intensities were then compared with a visual estimate of the intensities of the lines on the photographs. Table I gives the comparison of the calculated and observed intensities for different values of u for some

of the lines examined. The intensities of the higher angle lines are more sensitive to changes of u but unfortunately these lines were very faint. The parameter u would appear to lie between 0.21 and 0.25, the most likely value being 0.23 ± 0.01 .

The green material thus gave diffraction data which agreed closely with that of a substance having the formula Cs_2RhCl_6 , space group O_h^5 , isomorphous with $(\text{NH}_4)_2\text{PtCl}_6$, with four molecules per unit cell. From the values of the lattice and structure parameters the $\text{Rh}^{\text{IV}}-\text{Cl}$ distance is 2.3 Å.

Table II gives a comparison of lattice and structure parameters for other substances of this type.

TABLE II.
Comparison of Lattice Parameters, a , and Structure Parameters, u , for Crystals with Structure of Ammonium Chloroplatinate Type.

Crystal.	a (Å).	u .	R-X Distance (Å).
$(\text{NH}_4)_2\text{PtCl}_6^*$..	9.84	0.207	2.36
$\text{Cs}_2\text{GeF}_6^*$	8.99	0.20	1.80
$\text{K}_2\text{PtCl}_6^*$	9.73	0.240	2.33
$\text{K}_2\text{SnCl}_6^*$	9.93	0.245	2.43
$(\text{NH}_4)_2\text{PbCl}_6^*$..	10.14	0.23	2.33
$(\text{NH}_4)_2\text{SiF}_6^*$..	8.38	0.205	1.72
$(\text{NH}_4)_2\text{SnCl}_6^*$..	10.05	0.245	2.45
Cs_2RhCl_6	10.2	0.22 to 0.24	2.20 to 2.4

* Values taken from Wyckoff, "The Structure of Crystals", The Chemical Catalogue Co., New York, 1931.

SUMMARY.

Cæsium hexachloro rhodate III has been found to react with ceric nitrate in dilute nitric acid to yield a green insoluble material, cæsium hexachloro-rhodate IV. This compound has been examined by X-ray diffraction and found to be isomorphous with ammonium chloroplatinate, thus demonstrating that it is a compound of quadrivalent rhodium.

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Department of Chemistry,
 Sydney University and Technical College.

THE CHEMISTRY OF OSMIUM.

PART III. COMPLEXES OF TERTIARY ARSINES WITH BIVALENT AND TRIVALENT OSMIUM HALIDES.

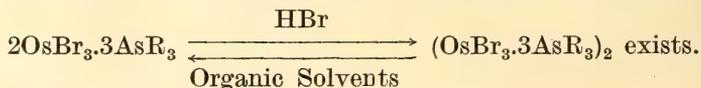
By F. P. DWYER, D.Sc.,
R. S. NYHOLM, M.Sc.
and B. T. TYSON.

Manuscript received, November 6, 1947. Read, December 3, 1947.

Very few complex compounds of bivalent or trivalent osmium have been described in the literature. This is due no doubt to the fact that both valency states have powerful reducing properties. The potential of the quadrivalent/trivalent osmium couple in hydrobromic and hydrochloric acids is 0.452 volt (Dwyer, McKenzie and Nyholm, 1945; Dwyer, Humpoletz and Nyholm, 1946), whilst the estimated potential of the trivalent/bivalent couple is probably as low as -0.2 volt. The stabilization of the powerfully reducing bivalent states of iridium and rhodium with tertiary arsines (Dwyer and Nyholm, 1941, 1942, 1943), however, suggested that stable complexes of bivalent and trivalent osmium might be obtained in a similar manner.

Quadrivalent osmium in the form of the hexahalogenates, R_2OsX_6 , failed to yield complexes with either tertiary arsines, tributyl phosphine, or diethyl sulphide. In the presence of halogen acids, tributyl phosphine acted as a base and salts of the type $(Bu_3P.H)_2OsX_6$ were isolated. The salts were sufficiently stable to be recrystallized from alcohol. This is surprising in view of the weakly basic nature of the alkyl phosphines, but salts of this type are not unique, for Burrows and Turner (1921) showed that tertiary arsines, which are even less basic, may yield salts of acids with large anions.

When the hexahalogeno osmates were refluxed with tertiary arsines for some time, the solutions changed colour due to reduction and the resulting trivalent osmium compound coordinated with excess of arsine to yield chloro and bromo compounds of the type $OsX_3 \cdot 3AsR_3$. These compounds crystallized well in pink or deep red needles, with sharp melting points, and were easily soluble in the usual organic solvents. The compounds failed to react with cold alcoholic silver nitrate, but on heating a precipitate of silver metal and silver halide resulted. The molecular weight of the tris-dimethylphenylarsine bromo compound was normal in benzene and the substances are accordingly the usual simple hexacovalent compounds, the analogues of the arsine complexes with trivalent ruthenium (Dwyer and Nyholm, 1946), iridium and rhodium. Like the rhodium compounds, tris-dimethylphenylarsine tribromo-osmium was found to exist in two forms. Although the two forms were monomeric in benzene, the evidence suggests that the compounds are not isomeric, since the high melting form is transformed into the lower melting form simply by dissolution in benzene, whilst the reverse change can be effected by solution of the lower melting form in alcohol in the presence of hydrobromic acid. It is probable that an equilibrium



It was not possible to determine the constitution of the proposed dimer, but three formulations are feasible: $[\text{Os}(\text{AsR}_3)_6][\text{OsBr}_6]$; $[\text{Os}(\text{AsR}_3)_5\text{Br}][\text{OsBr}_5(\text{AsR}_3)]$; and $[\text{Os}(\text{AsR}_3)_4\text{Br}_2][\text{OsBr}_4(\text{AsR}_3)_2]$.

It was not possible to isolate complexes of osmium tri-iodide and arsines, as in all cases the reduction proceeded to the bivalent state.

As with rhodium, iridium and ruthenium, the trivalent complexes were reducible with hot hypophosphorous acid to the paler coloured bivalent osmium compounds. The chloro and bromo compounds were of the form $\text{OsX}_{2.4}\text{AsR}_3$, and reduced alcoholic silver nitrate to the metal at room temperature. The deeply coloured iodo complexes, however, which were obtained simply by boiling the trivalent chloro or bromo compounds with hydriodic acid, were of the form $\text{OsI}_{2.3}\text{AsR}_3$, and like the rhodium II compounds probably contain iodine bridges to maintain hexacovalency. Attempts to prepare tetrakis arsine iodo compounds were fruitless.

The analysis of these osmium compounds was unsatisfactory in that a successful method of estimating either arsenic or osmium in the presence of each other and organic matter could not be devised. Analyses for carbon and hydrogen were also unreliable owing to the attack of osmium tetroxide formed during the combustion on the tap grease of the absorption tubes. The compounds were thus analysed only for halogen by the distillation method described in previous papers.

Attempts to prepare complexes of bivalent or trivalent osmium with tributyl phosphine or diethyl sulphide were unsuccessful.

EXPERIMENTAL.

Tris-Diphenylmethylarsine-Tri-Bromo-Osmium. Potassium hexabromoosmate (0.5 g.) was dissolved in hydrobromic acid (30 mls. of 3 N.), and heated to 80° C., and diphenylmethyl arsine (0.55 g., 3½ mols.) dissolved in hot alcohol (30 ml.) added. The mixture was refluxed for fifteen minutes, when the dark brownish red solution lightened to red, and a red crystalline precipitate commenced to form. The mixture was diluted with a little water and cooled. The impure material recrystallized from acetone melted at 176–178° and gave Br=14.3%. (Pure compound requires Br=20.65%.) This material was recrystallized twice from acetone, and finally fractionally precipitated from acetone with water. The least soluble fractions gave bright red needles, m.p. 205° and analysed correctly for the halogen. The substance was sparingly soluble in alcohol, but easily soluble in benzene and chloroform. An alcoholic solution heated with alcoholic silver nitrate gave a black precipitate of silver metal and silver bromide.

Found: Br=20.8; 20.9%. Mol. wt. cryoscopic in benzene, 1230. Calculated for $\text{OsBr}_3.3\text{Ph}_2\text{MeAs}$: Br=20.65%; mol. wt. 1162.

Tris-Dimethylphenylarsine-Tri-Bromo-Osmium, Low Melting Form. The preparation was repeated as above, substituting dimethylphenylarsine, and heating the mixture for only 5–6 minutes. The red crystalline precipitate formed on dilution with water was heated with alcohol when part dissolved. The alcoholic solution was then fractionally precipitated with water. The middle fraction gave red needles, m.p. 163°, easily soluble in alcohol, acetone and benzene. The molecular weight of the substance in benzene was normal, and the original material was obtained from the benzene after evaporation at room temperature. A solution of the substance in alcohol containing 5% of concentrated hydrobromic acid crystallized overnight to yield red needles and plates m.p. 173° of the higher melting form.

Found; Br=24.3%; mol. wt. 962. Calculated for $\text{OsBr}_3.3\text{PhMe}_2\text{As}$: Br=24.6%; mol. wt. 976.

Tris-Dimethylphenylarsine-Tri-Bromo-Osmium, High Melting Form. The portion of the preparation above which was insoluble in alcohol was dissolved in hot acetone and fractionally precipitated with water. The least soluble fraction gave red needles and plates, m.p. 173°, from aqueous acetone. The molecular weight in benzene was normal, but the material recovered

from the benzene by evaporation at room temperature melted at 163° and was soluble in alcohol. During the initial preparation of the substance larger yields can be obtained at the expense of the lower melting form by refluxing for a longer time.

Found: Br=24.4%; mol. wt. 970. Calculated for $\text{OsBr}_3 \cdot 3\text{PhMe}_2\text{As}$: Br=24.6%; mol. wt. 976.

Tris-Diphenylmethylarsine-Tri-Chloro-Osmium. Potassium hexachlorosmate (0.5 g.) in normal hydrochloric acid was heated to 80° C. and treated with diphenylmethylarsine (0.9 g., $3\frac{1}{2}$ mols.) in hot alcohol (30 ml.) and refluxed. The initially cloudy yellow solution became reddish after 20–25 minutes, and was diluted with water and cooled. The orange red oil which separated was treated with petroleum ether and allowed to stand overnight. The resulting pink solid was crystallized several times from dilute aqueous alcohol containing a little hydrochloric acid and gave finally pink needles, m.p. 120°. The substance was similar in properties to the bromide. Very poor yields were obtained in the preparation, and much potassium hexachlorosmate was recovered each time.

Found: Cl=10.4%. Calculated for $\text{OsCl}_3 \cdot 3\text{Ph}_2\text{MeAs}$: Cl=10.35%.

Tris-Dimethylphenylarsine-Trichloro-Osmium. Prepared as above in better yields, this substance crystallized well in pinkish-orange needles, m.p. 185°.

Found: Cl=12.7%. Calculated for $\text{OsCl}_3 \cdot 3\text{PhMe}_2\text{As}$: Cl=12.59%.

Tetrakis-Diphenylmethylarsine-Dichloro-Osmium. Potassium hexachlorosmate (0.4 g.) in 2 N. hydrochloric acid (30 mls.) was treated with diphenylmethylarsine (0.88 g., $4\frac{1}{2}$ mols.) in alcohol (20 mls.) and 30% hypophosphorous acid (2 ml.) added. The mixture, on heating, became reddish due to the formation of the osmium III complex, and then yellow as the reduction proceeded. The mixture was diluted considerably with water, and shaken with petroleum ether when a yellow sticky mass resulted. This was crystallized several times from dilute aqueous alcohol to give a pale yellow microcrystalline powder, m.p. 113°. The substance was very soluble in all organic solvents except petroleum ether. An alcoholic solution reduced alcoholic silver nitrate to the metal at room temperature.

Found: Cl=5.6%. Calculated for $\text{OsCl}_2 \cdot 4\text{Ph}_2\text{MeAs}$: Cl=5.7%.

Tetrakis-Dimethylphenylarsine-Dichloro-Osmium. Prepared in a similar manner to the compound above, the substance was a pale yellow micro-crystalline powder, m.p. 133–135°.

Found: Cl=7.1%. Calculated for $\text{OsCl}_2 \cdot 3\text{PhMe}_2\text{As}$: Cl=7.17%.

Tetrakis-Diphenylmethylarsine-Dibromo-Osmium. This was prepared in a similar manner to the chloro compound above, except that the reduction was stopped as soon as the red colour of the osmium III compound was discharged. The yields from various preparations were poor, and if the reduction was carried too far small amounts only of an unknown substance containing a low proportion of bromine and (probably) hypophosphite were obtained. After repeated crystallization from aqueous alcohol the substance was obtained as a brownish yellow powder, m.p. 100°.

Found: Br=11.9%. Calculated for $\text{OsBr}_2 \cdot 4\text{Ph}_2\text{MeAs}$: Br=12.05%.

Tetrakis-Dimethylphenylarsine-Dibromo-Osmium. Prepared in poor yield as the bromo compound above the substance was a brownish yellow powder, m.p. 131°.

Found: Br=14.9%. Calculated for $\text{OsBr}_2 \cdot 4\text{PhMe}_2\text{As}$: Br=14.84%.

Di-Iodo-Hexakis-Diphenylmethylarsine-Diodo-Diosmium. During attempts to prepare complexes of osmium tri-iodide by treatment of potassium hexachloro or hexabromo osmate with hydriodic acid and diphenylmethyl arsine it was noted that a mixture of compounds resulted as well as black osmium iodide. Finally an effort was made to replace the chlorine or bromine in the tris chloro or bromo arsine complexes with iodine by refluxing with purified hydriodic acid, in acetone solution. The result was a purplish black crystalline compound, which was crystallized fractionally from acetone. The least soluble fractions gave the correct analysis for a bivalent osmium complex with three coordinated arsine molecules, but the most soluble fraction was greenish in colour and gave I=32.6% ($\text{OsI}_3 \cdot 3\text{Ph}_2\text{MeAs}$ requires I=29.2%). Over a number of preparations the green substance gave values of iodine varying from 30% to 33%, and all efforts to purify or formulate the substance have failed. The dark purplish substance after many

crystallizations from aqueous acetone melted at 190° and gave a purplish solution in acetone, benzene and chloroform. On warming an alcoholic solution of silver nitrate was reduced to the metal.

Found: I=21.3%, 21.4%. Calculated for $(OsI_2 \cdot 3Ph_2MeAs)_2$: I=21.6%.

Di-Iodo-Hexakis-Dimethylphenylarsine-Diiodo-Diosmium. When tris-dimethylphenylarsine tribromo osmium in aqueous acetone solution was refluxed with hydriodic acid a mixture of substances was obtained. The least soluble fraction after fractional crystallization from aqueous acetone gave purplish black needles, m.p. 175°. This substance was apparently the analogue of the compound described above. No trace of the green compound was noted, and the intermediate fractions gave analyses for iodine intermediate between a compound of osmium II and osmium III.

Found: I=25.3%, 25.6%. Calculated for $(OsI_2 \cdot 3PhMe_2As)_2$: I=26.55%.

Hydrogen-Tri-n, Butyl-Phosphonium-Hexabromo-Osmate. Potassium hexabromo osmate (0.5 g.) was dissolved in hydrobromic acid (30 ml., 3 N.) and treated with tributyl phosphine (0.6 g., 3 mols.) in alcohol (30 ml.). The mixture was heated to 80°, when a red crystalline precipitate came down. The substance after recrystallization from alcohol melted at 171°. If the original preparative mixture was heated for more than a few minutes the red substance decomposed and the phosphine was oxidized to the phosphine oxide.

Found: Br=44.1%. Calculated for $((C_4H_9)_3H.P)_2 \cdot OsBr_6$: Br=44.47%.

Hydrogen-Tri-n, Butyl-Phosphonium-Hexachloro-Osmate. Prepared as the bromo compound above this gave a bright yellow crystalline powder, soluble in alcohol and acetone, m.p. 158°.

Found: Cl=26.5%. Calculated for $((C_4H_9)_3H.P)_2 \cdot OsCl_6$: Cl=26.4%.

SUMMARY.

Like ruthenium, osmium IV in the form of the hexahalogenates fails to yield complexes with tertiary arsines, which first reduce the element to the trivalent state, and then form simple unbridged, hexacovalent complexes of the type $OsX_3 \cdot 3AsR_3$. Reduction of these compounds with hypophosphorous acid leads to the formation of osmium II complexes of the forms $OsX_2 \cdot 4AsR_3$ and $(OsI_2 \cdot 3AsR_3)_2$.

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THE COLORIMETRIC ESTIMATION OF STRYCHNINE.

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The importance of having available methods for the estimation of small quantities of potent alkaloids such as strychnine cannot be stressed too much. Owing to the small dosage of this substance, most methods for control in the manufacture of hypodermic injections and tablets require rather large amounts of material. Hypodermic tablets of strychnine are made in strengths varying from 1/20th to 1/100th grain, generally as sulphate, so that for the usual volumetric analysis from 20 to 100 tablets may be required. This number may be readily at hand during manufacture, but once distributed, a definite restriction appears in the amount available for assay. Also, the result thus obtained represents an average content, and for closer control in the mixing of medicament and base, the analysis of single tablets is useful. In these circumstances, colorimetric processes become of value.

Both reduction and oxidation procedures have been suggested for the determination of small amounts of strychnine. Malaquin (1909) introduced a characteristic reaction, which consisted of reduction by granulated zinc and hydrochloric acid, a rose red colour then being produced with sulphuric acid. Denigès (1911) modification of this test, reduction with zinc amalgam in a boiling water bath followed by treatment with sodium nitrite, was used by Allport and Jones (1942) for the examination of hypodermic tablets and by Allen and Allport (1940) for preparations of *nux vomica*.

Oxidation tests are more simply carried out and have been used for the identification of the alkaloid. Mandelin's reagent—solution of ammonium vanadate in sulphuric acid—has been suggested by Scandola (1911) for the estimation of small quantities. This reagent was tried during the present work but suffers from several disadvantages. When strychnine is treated with oxidizing agents such as ammonium vanadate, potassium dichromate, etc., in sulphuric acid, it passes through several colour changes. First, there is obtained a very intense purple colour which gradually fades and is replaced by more reddish shades, and the final colour is cherry red. Since this reagent itself is rather deeply coloured (reddish orange), the different colour changes during oxidation of small quantities may be masked to a large extent. Thus it is unsuitable for the technique employed in the present method. Garratt (1937) has suggested triturating small residues of strychnine with a large excess of solid ammonium vanadate and a few drops of sulphuric acid. Under these conditions it is difficult to ensure good contact and the procedure generally offers little advantage over the solution of the oxidizing material.

Cerium oxide is another oxidant commonly used. This occurs as brown material only slightly soluble in sulphuric acid, and although very useful for qualitative purposes, is generally unsuitable for quantitative work.

Ceric sulphate, however, is available as a clean, orange substance, readily soluble in water. It is not very soluble in sulphuric acid, but, on warming, sufficient dissolves to give a solution which is only faintly coloured, and which gives strong tests with small amounts of strychnine. By standardizing the

amount of reagent and the time allowed for the reaction, the use of this reagent for colorimetric estimations becomes possible. The reagent is very sensitive and a range of standard colours with a lower limit of 0.005 mg. strychnine may be used in the very simple procedure described below.

EXPERIMENTAL.

(a) Reagents.

- (i) *Solution of ceric sulphate in sulphuric acid.* Ceric sulphate, 1.0 g., powdered and warmed on steam bath for 20-30 minutes with sulphuric acid, 100 ml., stirring occasionally. Excess ceric sulphate is then removed by allowing to settle or by centrifuging. The finer particles settle rather slowly and even after centrifuging, the solution may be slightly turbid with suspended material. However, it may be used if not quite clear, provided, of course, the distribution of insoluble material is maintained during the estimation.
- (ii) *Strong solution of strychnine.* Strychnine 0.1 g., dissolved in chloroform 100 ml. (1 ml. = 1 mg. strychnine).
- (iii) *Dilute solution of strychnine.* Prepared by diluting 1 volume of strong solution to 10 volumes with chloroform (1 ml. = 0.1 mg. strychnine).

(b) Preparation of Standards.

Gently evaporate to dryness over a steam bath in small porcelain crucibles, about 15 ml. capacity, amounts of dilute solution of strychnine ranging from 0.1 to 1.0 ml. (0.01-0.1 mg.). To each residue, when cool, add solution of ceric sulphate, 2 ml. (Add the reagent to standards and unknown without stirring.) Briskly stir the contents of each crucible with a small glass rod for a few seconds at a time so as to develop the range of colours as far as possible at the same time. Compare unknown and standards after 2-3 minutes colour development for preliminary estimation. Allow to stand 10-15 minutes and make final comparison. Perform a blank experiment.

DISCUSSION OF METHOD.

(a) *Colour of Blank.* While there is a very slight yellow colour in the blank due to the reagent, the colour from as little as 0.005 mg. strychnine is easily distinguishable.

(b) *Colour Changes.* On stirring, the colour in each crucible soon becomes purple, with greater intensity in those containing the larger amounts of strychnine. The introduction of reddish tints then begins, and since these appear more rapidly with smaller amounts of strychnine, in the interval of 2-3 minutes after addition of the reagent, there is a range of colours from more or less reddish solutions with little purple to those still containing a considerable proportion of purple which are also more intense in colour. In all cases the purple colour disappears completely on further standing and finally there is a range of intensity in the same reddish orange colour. The reagent appears to deteriorate on keeping and ultimately loses its faint yellow colour. This leads to a variation in the rate of colour change so that the time periods given above may vary slightly according to the age of the reagent.

(c) *Colour Comparison.* As mentioned, use is made of the initial series of colours for an indication of the amount of alkaloid present. The strongest colour is at the purple stage, and the method would be even more sensitive if the reaction could be stopped at this point.

The final reddish orange colours are more readily compared at the lower end of the range, up to 0.5 ml. of dilute solution of strychnine, and it is suggested that for larger amounts a repeat experiment with a smaller aliquot be performed, also using fewer standards, so that the colours develop more evenly. The larger

amounts may possibly be more readily matched after diluting to 5 ml. with sulphuric acid and transferring to half-inch test tubes.

(d) *Determination of Amount of Material to be Used.* With a little practice it is not necessary to prepare a complete range of standards. It is possible to use the initial purple intensity to determine whether a smaller aliquot would be desirable to bring the final colour to the more sensitive portion of the range.

(e) *Stability of Colour.* The final colour fades on keeping, but the relative intensities are maintained for some time. A series of experiments was performed in which the coloured solution was diluted with water. Although a range of colour was obtained, it was not as permanent as when left in concentrated acid.

(f) *Stirring.* With the small amounts of strychnine present, efficient stirring is necessary to bring the film of alkaloid into contact with the reagent. The short periods of stirring should be continued at least until the reddish shades appear.

(g) *Interfering Materials.* Separation from the lactose of hypodermic tablets is necessary, as this affects the ceric sulphate.

The method is also subject to the usual interferences with oxidation tests for alkaloids.

(h) Porcelain crucibles provide a good background for the comparison of colours.

PROCEDURE FOR HYPODERMIC TABLETS.

Dissolve one tablet in distilled water, 5 ml., in a small separator, 25 ml. capacity. Add chloroform, 10 ml., make alkaline with dilute solution of ammonia, and shake vigorously during several minutes for extraction. Allow the layers to separate and filter the chloroform layer through a small plug of cotton wool, previously washed with chloroform, into a 25 ml. graduated flask. Continue the extraction with two further quantities of chloroform, 10 and 5 ml. respectively, passing these in turn through the filter. Finally, adjust the volume to 25 ml. with more chloroform. One ml. of this solution is evaporated and treated as described.

The range of standards above will just cover hypodermic tablets of strengths ranging from 1/20th to 1/100th grain of strychnine, as sulphate, using the dilutions suggested. For strengths above 1/40th grain it is preferable to reduce the amount of solution used to 0.5 ml.

EXAMINATION OF TABLETS.

Tablets of three strengths from one manufacturer were examined with the results summarized in the following table :

Labelled Strength as Strychnine Sulphate.	Equivalent in Strychnine Alkaloid.	Volume of Final Solution Used in Assay.	Equivalent of Dilute Solution of Strychnine.	Total Amount of Strychnine Found.
1/60th grain ..	0.84 mg.	1.0 ml.	0.30 ml.	0.75 mg.
1/40th " ..	1.26 mg.	1.0 ml.	0.45 ml.*	1.12 mg.
1/30th " ..	1.68 mg.	0.5 ml.	0.30 ml.	1.50 mg.

* This result obtained by interpolation.

SUMMARY.

A method is presented for the estimation of small quantities of strychnine, based on the colour produced by the action of ceric sulphate in sulphuric acid, and a procedure suggested for the examination of hypodermic tablets.

The method has been applied to the examination of hypodermic tablets.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD.

PART I. GEOLOGY OF THE WILLOW TREE DISTRICT.

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With Plate VII.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The North-Western Coalfield of New South Wales comprises an area extending from the Nandewar Mountains, north-east of Narrabri, to the vicinity of Blandford, a distance of approximately 150 miles.

The geological survey of the coalfield was included in the programme of the New South Wales Geological Survey. Field work commenced in 1945 and has been proceeding continuously during field seasons since that date. A considerable amount of field work still remains to be completed. The work has been concentrated on the study of the Permian rocks, formations of other ages being studied only in so far as was necessary to map the boundaries of the Permian system and elucidate the structural geology of the area.

It is proposed to publish the work in a series of papers, based on reports made to the New South Wales Department of Mines, dealing with different sections of the area. Although the bulk of the work carried out so far has been centred on the Gunnedah-Curlewis district, the geology of the Willow Tree district is being published first because it provides the clue to the correlation of the Permian Sequence of the North-Western Coalfield with the type area in the Hunter Valley.

TOPOGRAPHY AND ACCESS.

Willow Tree is 1,390 feet A.S.L. and is situated in the County of Buckland on the New England Highway and the Great Northern Railway Line, being 233 miles by rail from Sydney. The area shown on the Geological Map of the Willow Tree district (Plate VII) extends about $2\frac{1}{2}$ miles in a north-westerly and south-easterly direction and is about one mile wide. Relief is moderate, the highest point surveyed being 570 feet above the level of the railway station or 1,960 feet A.S.L.

The central portion of the area is occupied by the valley of Borambil Creek, which has been eroded on the softer Permian rocks. The south-western edge is occupied by a line of hills composed of Triassic rocks capped in places by Tertiary basalt. Carboniferous rocks occupy a corresponding line of hills to the north-east.

The survey was carried out by means of a telescopic alidade and plane table. Contours at intervals of 50 feet are shown on the Geological Map of the Willow Tree district (Plate VII).

GEOLOGY.

The geological formations comprise the following :

Tertiary to Recent		Alluvium.
Tertiary		Basalt flows and dykes.
Triassic		Conglomerates and sandstones.
Permian—		
Borambil Series	{ Upper Stage { Lower Stage	{ Soft claystones, sandstones, con- glomerates and thin limestone bands. { Sandstones and conglomerates with Upper Marine fossils.
Willow Series	{ Upper Stage { Werrie Stage { Lower Stage	{ Shales, sandstones, conglomerates and coal seam. <i>Glossopteris</i> present. { Mainly amygdaloidal basalts. Sandstones, shales, tuffs, con- glomerates and carbonaceous beds. <i>Glossopteris</i> present.
Carboniferous—		
Upper Kuttung	Upper Glacial Stage	Conglomerates, varves, tuffs.

The rocks will now be described in detail, commencing with the oldest.

Carboniferous.

The only Carboniferous rocks mapped form a small outcrop in the north-eastern section of the area. They comprise the uppermost beds of the Upper Glacial Stage of the Upper Kuttung as described by Carey (1934, 1937) in connection with the geology of the Werrie basin. They consist of fluvio-glacial conglomerates, varves and a thin bed of tuffs which is probably the topmost bed of the Carboniferous system, although it could be the basal bed of the Permian. Micro-sections of the tuffs show excellent examples of shards.

Permian.

The discovery of Upper Marine fossils in sandstones outcropping along Borambil Creek has rendered necessary a complete reclassification of the Permian strata of the Willow Tree area. Owing to some uncertainty in the correlation with the Hunter Valley sequence and the unsuitability of the terminology for application to the Willow Tree strata, it is considered advisable to give the series local names, and the classification shown above is suggested. It is proposed to describe the sequence first and leave the discussion of the correlation until later.

Willow Series. This series consists of two groups of freshwater sediments separated by a considerable thickness of lava flows. It has been divided into three stages which are shown below, together with their probable thicknesses.

Upper Stage	.. More than 1,050 feet	} 3,450 feet
Werrie Stage	.. Less than 2,400 feet	
Lower Stage	.. 300-550 feet	
Total thickness	.. 4,000 feet	

The Lower Stage consists of sandstones, shales, tuffs, conglomerates and carbonaceous beds. They are continuous with rocks mapped by Carey (1934, 1935) in the Werrie Basin, from which he recorded the presence of the *Gangamopteris-Noeggerathiopsis* flora. He and Raggatt (1932) recorded the occurrence of coal seams in the beds at Currabubula and in the parishes of Quirindi, Coeypolly and Werrie, County of Buckland.

There is no sharp line of demarcation of the top of the Lower Stage, the uppermost strata being interbedded with flows of amygdaloidal basalt belonging to the Werrie Stage. This stage is the southerly continuation of the Werrie basalts mapped by Carey.

The boundary between the Werrie and Upper Stages of the Willow Series is entirely obscured by the alluvium along Borambil Creek. The section of the Upper Stage available for examination comprises about 900 feet of the topmost beds which outcrop along the south-western bank of Borambil Creek. A coal seam of good quality, probably at least 10 feet thick was struck in a well shown on Plate VII. The strata exposed consists of shales, sandstones, grits and conglomerates and contain bands of concretionary ironstone. Impressions of *Glossopteris* are plentiful.

Borambil Series. This series has been so named because of its occurrence along and to the west of Borambil Creek and has been divided into two stages.

The Lower Stage consists of sandstones and conglomerates and shows current bedding in places. On one horizon the following suite of fossils has been found :

Spirifer sp. indet.

Spirifer duodecimcostata McCoy.

Spirifer vespertilio Sowerby.

"*Martiniopsis subradiata*" Sowerby (large var.).

Merismopteria macroptera (Morris).

Deltopecten subquinquelineatus Eth. and Dun.

Pelecypod (internal cast) indet.

The stage appears to be somewhat lenticular, the maximum thickness being 350 feet.

The Upper Stage is at least 2,000 feet thick and is composed of soft claystones, sandstones, conglomerates and thin beds of limestone. The latter are concretionary, at least in part, and may be equivalent to the calcareous concretions found at different horizons in the Mulbring Stage of the Upper Marine (Raggatt, 1929*b*; Morrison and Raggatt, 1928). The rocks are soft, easily eroded and form poor outcrops. No fossils have been found in this stage and it is impossible to state definitely whether they are of marine or freshwater origin.

There is a small isolated outcrop of soft clayey and carbonaceous beds beneath the Triassic cliffs at the head of the main branch creek north of Oaklyn Homestead. They may be distinct from the Upper Stage of the Borambil Series, but have been included with them for mapping purposes.

Correlation.

Previous workers (Carey, 1934, 1935; Raggatt, 1938*a*) classified all the sediments overlying the Werrie basalts (Borambil Series and Upper Stage of the Willow Series) as Upper Coal Measures, the basalts themselves as Upper Marine and the underlying freshwater sediments as Lower or Greta Coal Measures, although Carey (1935) discussed the possibility that the last may correspond to an horizon in the Lower Marine Series.

The key to the correlation with the Permian Sequence of the Hunter Valley is provided by the marine fossils discovered in the Lower Stage of the Borambil Series. It is not possible to give an exact correlation of the fossiliferous horizon with the Upper Marine sequence of the type area. The lithology of the rocks would favour correlating them with either the Muree or Branxton Stages. However, Mr. H. O. Fletcher states: "The facies of the marine fossils indicates a geological age fairly high in the Upper Marine Series of the Permian." In the absence of fossil evidence on which to base an opinion, the correlation of the

Upper Stage of the Borambil Series must be doubtful, but it is considered that it is probably equivalent in part to the Mulbring Stage of the Upper Marine, and in part to the Tomago Stage of the Upper Coal Measures.

The outcrop of clayey and carbonaceous rocks referred to above may be an integral part of the Upper Stage of the Borambil Series or may represent part of the Newcastle Stage of the Upper Coal Measures, immediately underlying and conformable with the Triassic rocks.

The Upper Stage of the Willow Series is the equivalent, at least in part, of the Lower or Greta Coal Measures. However, because of the doubt as to the exact position of the fossiliferous horizon in the Upper Marine sequence and the possibility that some of the *Glossopteris*-bearing sediments may be a freshwater equivalent of portion of the Upper Marine of the Hunter Valley, it is considered preferable to refer to the sediments as the Upper Stage of the Willow Series. In the Cessnock district the Greta Seam forms the topmost bed of the Lower Coal Measures, which range in thickness from 100 to 300 feet (Jones, 1939). The roof of the coal seam at Muswellbrook is 75 feet from the top of the Lower Coal Measures and the total thickness of Greta sediments is 370 feet (Raggatt, 1929*a*). At Willow Tree, if we assume that there has been no normal strike faulting or igneous intrusives which are obscured by the alluvium along Borambil Creek, the coal seam is at least 1,050 feet from the top of the Upper Willow Stage and the total thickness of the stage probably greater than this figure. Any thrust faulting present would increase these estimates. The conditions could be explained by considering the top portion of the Upper Willow Stage as being a freshwater equivalent of part of the Upper Marine of the Hunter Valley or by an increase in thickness of the Greta sedimentation. In the latter alternative the Willow Tree coal seam may also be a separate seam developed at a much lower horizon than the Greta Seam.

David (1907) records from the Seven Mile near Raymond Terrace the occurrence of freshwater sediments, which contain abundant tuffaceous bands and a coal seam, and which underlie a thick formation of amygdaloidal basalts. He assigned them to the Lower Marine, and the writer considers that the Permian freshwater sediments and the overlying Werrie Basalts at Willow Tree are approximately on similar horizons. Browne and Dun (1924) also record the presence of a sandstone formation, tuffaceous in appearance, underlying amygdaloidal basalt near Lochinvar. The authors state that "The lower parts contain indeterminate plant stems and it was from the upper portions, which are in places pebbly, that the marine fossils were obtained". A similar relationship is found in the Loder's Mount area (to be described in Part II of the Geology of the North-Western Coalfield), where Lower Marine fossils have been found in the topmost beds of the stage. Amygdaloidal basalts which were probably contemporaneous with the above also occur in the Muswellbrook and Wingen-Murrurundi districts. The Lower Marine Basin probably occupied much the same area throughout the whole of the Lower Marine time, but the proportion of the basin which was open to the sea varied considerably. At times considerable areas would appear to have been occupied by freshwater lakes, although some of the plant-bearing horizons, particularly where the plant remains are fragmentary and could have been carried into the sea, may have been laid down under marine conditions. Basalt flows were poured into the basin throughout the whole of the area under consideration and the greater thickness of basalts in the Werrie Basin may be due to the continuation of volcanic activity in that area while sedimentation was proceeding in the Lower Hunter Valley.

Triassic.

Only the basal portion of the Triassic System was examined. It consists of coarse conglomerates which are interbedded with fine conglomerates and sandstones. It is characterised by the presence of abundant jasper pebbles and is similar to the basal portion of the Triassic as exposed throughout the North-Western Coalfield in sections already surveyed in detail.

Tertiary.

Tertiary basalt occurs as a capping to the line of hills along the south-western edge of the area mapped. It overlies the Triassic rocks and in places obscures completely the junction between the Triassic and Permian rocks. It also occurs as isolated outcrops and as dykes in the Permian rocks.

Tertiary to Recent.

The alluvium along Borambil Creek consists of black sticky clay containing gravel beds which yield good supplies of underground water at shallow depths. It has been derived mainly from the weathering of the Werrie and Tertiary basalts of the neighbourhood.

STRUCTURAL GEOLOGY.

The structural geology of the area is extremely interesting. For a full discussion it would be necessary to consider neighbouring areas, and the present discussion will be confined to the area mapped.

A cross-section of the area is shown in Plate VII. The portion beneath the Triassic rocks can be regarded as diagrammatic only.

Broadly speaking, the area surveyed may be regarded as being situated on the south-western limb of an anticline, whose axis trends in a north-westerly direction. The core of the anticline consists of Carboniferous rocks and the flank of Permian sediments. On the eroded edges of the latter the Triassic beds were laid down unconformably.

On the hill in the north-eastern corner of Plate VII the dips in the Carboniferous are low, being about 12° . Proceeding in a south-westerly direction the dips steepen until the Lower Stage of the Willow Series, which dips at about 55° , is reached. The dip continues to steepen until it reaches about 65° , and with few exceptions all outcrops between this point and the Triassic rocks dip at this angle or more steeply. Vertical dips are common and in places the beds are overturned; in one place a dip of 70° in the opposite direction was measured.

It was impossible to measure the dip of the clayey and carbonaceous beds at the head of the main branch creek north of Oaklyn Homestead. It is, therefore, impossible to state whether they dip in conformity with either the Borambil Series or the overlying Triassic rocks.

To what extent the sediments are affected by strike faulting in the section occupied by the Werrie Basalts and the alluvium along Borambil Creek it is impossible to say. It has certainly been affected by oblique faults which trend parallel to thrust faulting further to the north-east and are related to it.

An outcrop of finely bedded shaley sandstones occurs beneath the alluvium in the bed of the main creek north of Oaklyn Homestead and dips to the north-east at 35° . It is bounded on the south-west by a fault and on the north-east by creek alluvium. It probably represents portion of a block which has been caught between two faults, thus accounting for the anomalous dip.

The Triassic rocks have a general dip in a south-westerly direction which averages about 15° . They cross the line of the strike of the Borambil Series in the northern section of the area mapped and the isolated outcrop of Triassic

conglomerate in this section is surrounded on three sides, at least, by vertically dipping Permian strata. It is considered impossible to explain the relationship of the Triassic to the Borambil Series without postulating an almost right-angled unconformity between those formations.

It is considered that the folding of the Permian and Carboniferous at Willow Tree took place before the close of Upper Coal Measures time because the degree of unconformity existing between the Permian and the Triassic would require a period of erosion prior to the deposition of the latter. Also the outcrop of clayey and carbonaceous beds at the head of the main creek north of Oaklyn Homestead may be conformable with the Triassic rocks and represent portion of the Newcastle Stage.

In connection with the determination of the lower limit of the commencement of the folding, the first manifestation of the late Palaeozoic diastrophism was recorded by David (1907), who observed the fact that the folding of the Lochinvar anticline commenced at the end of Muree time. However, at Willow Tree there is at least 2,000 feet of strata lying apparently conformably above what may be the equivalent of the Muree.

Raggatt (1938*b*) considered that Mulbring and Tomago time together represented a period of quiescence between the commencement of folding in Muree time and uplift of the surrounding land which he considered took place in Newcastle time. The writer has observed an interesting structure in a cutting on the Pelaw Main railway line at the point where it is crossed by the East Maitland-Mulbring Road. The Tomago Coal Measures west of the tunnel and in a small section near the base of the cutting east of the tunnel dip at about 35° - 40° , while the remainder of the sediments east of the tunnel dip at approximately 10° . The main portion of the junction between the two groups of sediments is obscured by the tunnel, but where visible dips at about 10° and is parallel to the bedding of the overlying sediments. The lowest bed of the more flatly dipping sediments contains small pebbles near its base and appearances favour regarding the relationship as an unconformity. If it is due to faulting it would be in the nature of a low angle overthrust which shows no signs of dragging the underlying sediments along the thrust plane in the section exposed. If the section represents a local unconformity situated not far below the accepted junction between the Tomago and Newcastle stages of the Upper Coal Measures, it would show that some folding of the Permian took place at that time and would furnish additional evidence on which to base an estimate of the age of the commencement of folding at Willow Tree.

It is considered that the folding probably commenced about the beginning of the Newcastle age. However, all the faulting did not take place in the pre-Triassic time because the Triassic and Lower Jurassic (Lower Comiala) in the vicinity of Murrurundi are dragged up against the Carboniferous, along a thrust fault, until they are dipping nearly vertically.

At Willow Tree there appears to have been minor normal faulting, probably during Tertiary time, along the margin of the Triassic rocks, which explains the outcrops of Triassic conglomerate below the general level of the main Triassic conglomerates further west. On Plate VII the fault has only been shown on the northern section of the map. It probably continues along Toll Bar Ridge east of the main mass of Triassic conglomerate and would explain the occurrence of abundant Triassic conglomerate pebbles on a number of hills below the level of the main outcrop and separated from it in many instances by a saddle. It was thought preferable not to show the fault continuing further to the south because its exact location is somewhat doubtful, and although Triassic conglomerate pebbles are very abundant on the hills, actual outcrops are wanting in most instances.

The unconformity between the Triassic and Permian is regarded as being only of local occurrence and marking approximately the position of the Triassic shoreline. It is considered that the dips in the Permian would quickly flatten in a south-westerly direction, the Newcastle stage of the Upper Coal Measures would progressively increase in thickness, and the Triassic and Permian would have their usual conformable relationship.

ACKNOWLEDGEMENTS.

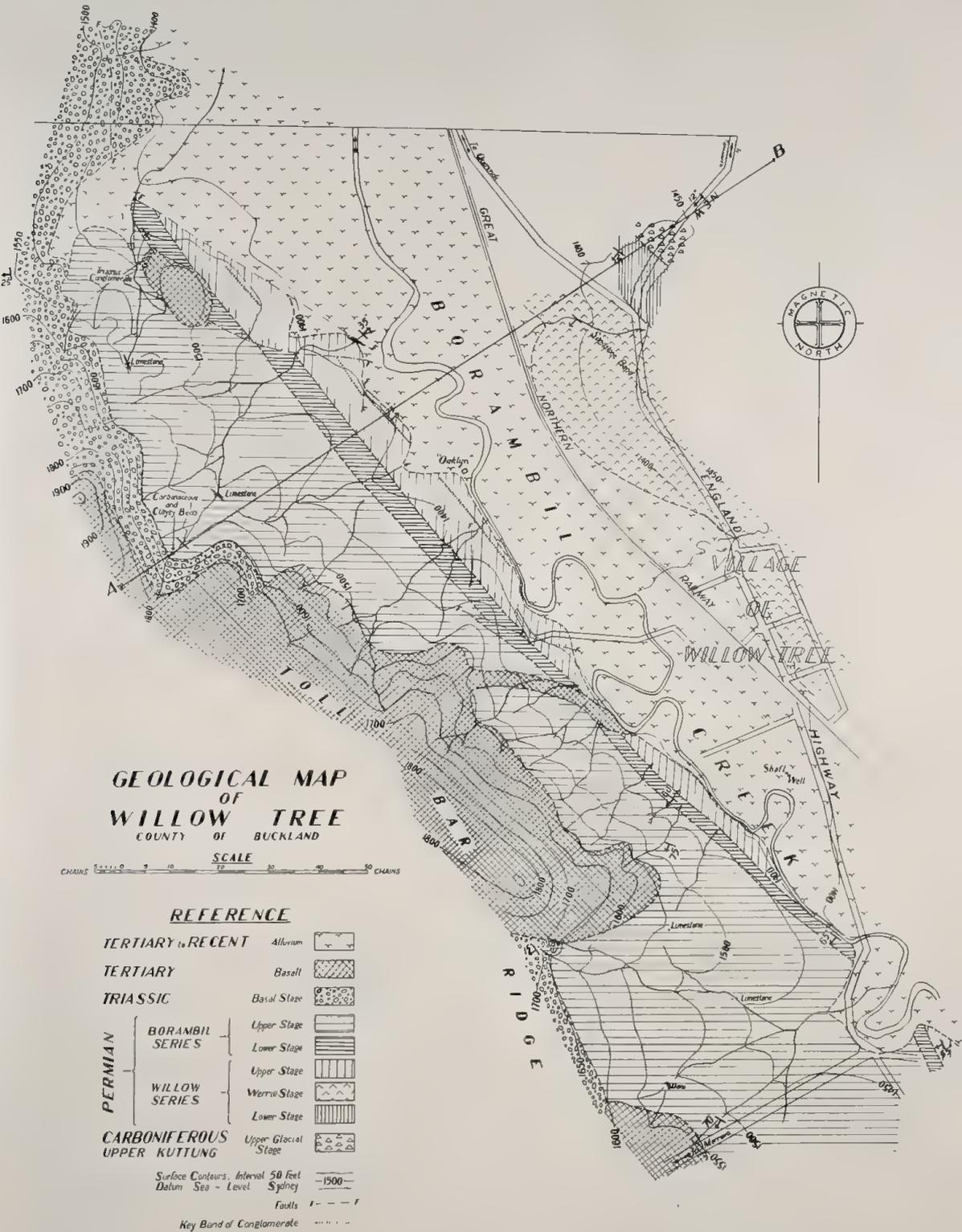
I was assisted on the present survey by Mr. J. C. Lloyd, B.Sc., who was responsible for the instrumental work in connection with the alidade survey, and drafting of the plan to accompany this paper. Many helpful discussions with him on points raised during the progress of the survey are gratefully acknowledged. I am indebted to Mr. H. O. Fletcher, of the Australian Museum, for the determinations of the Upper Marine fossils. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

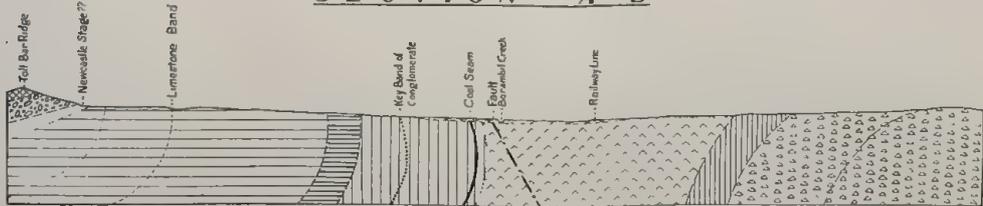
The Permian rocks of the Willow Tree area form the south-western flank of an anticline whose core consists of Carboniferous strata. The Permian probably comprises the equivalents of the Lower Marine sediments (represented by freshwater beds) and lavas, Lower Coal Measures, Upper Marine and Tomago Stage. They were probably folded prior to the deposition of the Newcastle Stage. The Triassic was laid down unconformably on the eroded edges of the Permian strata along the south-western boundary of the area. It is considered that the degree of unconformity would lessen markedly in a south-westerly direction and the relationship between the Triassic and Permian would become conformable.

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SECTION A-B





GEOLOGY OF THE NORTH-WESTERN COALFIELD.

PART II. GEOLOGY OF THE WILLOW TREE-TEMI DISTRICT.

By F. N. HANLON, B.Sc., Dip.Ed.

Geological Survey of New South Wales.

With Plate VIII.

(Presented by permission of the Under Secretary for Mines.)

Manuscript received, November 19, 1947. Read, December 3, 1947.

INTRODUCTION.

The Liverpool Range forms the southern and eastern boundary of the Willow Tree-Temi area. To the north of Willow Tree it adjoins the Werrie Basin mapped by Carey (1934, 1935, 1937). It includes the Willow Tree area, the geology of which was described in Part I of the Geology of the North-Western Coalfield (Hanlon, 1947).

The survey was in the nature of a close reconnaissance and the more detailed work has been confined mainly to the Permian system.

TOPOGRAPHY AND ACCESS.

The area is situated entirely within the south-eastern part of the County of Buckland and comprises the Parish of Temi, with portions of the Parishes of Loder, Quirindi and Warrah and the Warrah Estate. It is traversed by the New England Highway and the Main Northern Railway Line. Ardglen, adjacent to the Liverpool Range, is 226 miles by rail from Sydney, and Willow Tree is 233 miles. Access by roads to some sections are good, while others are accessible only by horse or on foot. Many roads shown on the parish maps either do not exist, or if ever constructed are now untrafficable.

Topographic relief is considerable. The lowest section of the district is adjacent to Willow Tree, which is less than 1,400 feet above sea level, while Mt. Temi, or Bother Jimmy as it is known locally, is approximately 4,113 feet A.S.L. The positions of creeks, particularly small tributary creeks, shown on the parish maps are inaccurate in most instances and on the geological map to accompany this paper (Plate VIII) the positions of many of them have been replotted. This has been done particularly in the portions of the Parishes of Temi and Loder, in which Permian strata outcrop.

Generally speaking, the more elevated sections of the area are occupied by Tertiary igneous rocks or Carboniferous strata, the lower lying sections consisting of the Permian beds.

GEOLOGY.

The classification adopted in Part I of the Geology of the North-Western Coalfield (Hanlon, 1947) is retained. It comprises the following formations which are described in detail below, commencing with the oldest.

Tertiary to Recent.

Tertiary.

Triassic.

Permian—

Borambil Series.

{ Upper Stage
{ Lower Stage

Willow Series.

{ Upper Stage
{ Werrie Stage
{ Lower Stage

Carboniferous—

Upper Kuttung Series.

Upper Glacial Stage

Carboniferous.

The survey was not directly concerned with the Carboniferous stratigraphy and it was not studied in any great detail except in the northern part of the area mapped, where it was necessary in order to trace the positions of some of the faults shown.

The strata belong to the Upper Glacial Stage of the Upper Kuttung as described by Carey (1934, 1937) in connection with the geology of the Werrie Basin. They consist of fluvio-glacial conglomerates, varves, tuffs and acid lavas. The varves in places show very sudden lateral variation into conglomerates, the change being so sudden at times as to resemble a faulted junction.

Where developed, acid lavas or tuffs seem to form the top of the Carboniferous system. However, these beds are lenticular and in many places the Permian strata are resting directly on either conglomerates or varves.

Permian.

The conclusions reached previously (Hanlon, 1947) as to the age of the various stages of the Permian strata might be stated briefly here. The Lower Stage of the Borambil Series consists of sandstones and conglomerates with Upper Marine fossils. The Upper Stage comprises soft claystones, sandstones and conglomerates with thin limestone bands, and is unfossiliferous. It is probably equivalent in part to the Mulbring stage of the Upper Marine and in part to the lower portion of the Upper Coal Measures. The Borambil Series is found only at Willow Tree. It has been described previously (Hanlon, 1947) and the description will not be repeated here. The Willow Series is considered to be equivalent to both the Lower Coal Measures and the Lower Marine Series of the Hunter Valley. It will be described now.

Willow Series.

The Upper Stage consists of shales, sandstones, grits and conglomerates and contains bands of concretionary ironstone, as well as a seam of good quality coal, at least 10 feet thick. Details of the occurrence of the coal seam have been given by Raggatt (1938). This stage only outcrops in the Willow Tree area and its correlation with the type area has already been dealt with (Hanlon, 1947). It was considered to be equivalent, at least in part, if not entirely, to the Greta or Lower Coal Measures.

It is underlain by the Werrie Stage, which consists mainly of amygdaloidal basalts. The lower portion is interbedded with sediments of the Lower Stage

of the Willow Series. The latter consists of sandstones, shales, tuffs, conglomerates and carbonaceous beds and is continuous with rocks mapped by Carey (1934, 1935) in the Werrie Basin, from which he recorded the presence of the *Gangamopteris-Noeggerathiopsis* flora. Although the beds contain plentiful plant remains, the only identifiable fragments consist of *Glossopteris*. The oil-shale, known as the Temi or Doughboy Hollow deposit, occurs within this stage. It has been described in some detail by David (1892) and Carne (1903). Both Raggatt (1932) and Carey (1935) record the presence of coal seams in the beds at Currabubula and in the Parishes of Quirindi, Coeypolly and Werrie, County of Buckland.

There is a local development of sediments composed of sandstones, grits, conglomerates, tuffs and agglomerates in the Temi Basin. In the vicinity of Loder's Mount there are three main groups, which are separated by flows of Werrie Basalts. Further south at the Devil's Pinch near Mt. Temi, the intervening basalts have largely lensed out. Rather than draw a boundary at the base of the lowest basalt flow and include the sedimentary bands in the Werrie Stage, or include some of the basalt flows in the Lower Stage by drawing the boundary at the top of the highest sedimentary band, it was thought preferable to map the individual sedimentary beds as belonging to Lower Stage and the lava flows as belonging to the Werrie Stage in order to delineate the structure more clearly.

Intrusive and extrusive masses of Tertiary basalt in the vicinity of Mount Temi and Jack White's Mountain have rendered accurate mapping of the Lower and Werrie Stages of the Willow Series in that locality very difficult. The area shown as Tertiary basalt between the basal substage and the beds outcropping at the Devil's Pinch probably consists of Werrie Basalts in part, but in the time available for the survey it was impossible to make any separation.

An interesting suite of marine fossils was collected from the topmost bands of Lower Willow sediments on the slopes of Loder's Mountain. The fossils were kindly identified for me by Mr. H. O. Fletcher, of the Australian Museum, who favours assigning them to about the middle of the Lower Marine Series. The list of fossils determined is as follows:

Spirifer sp. indet.

Spirifer cf. *stokesi* Konig.

"*Martiniopsis subradiata*" Sowerby (small var.).

Stutchburia farleyensis Etheridge.

Eurydesma cordata Morris.

Aviculopecten mitchelli Eth. and Dun.

Platyschisma ocula Sowerby.

Taking all the evidence into consideration it seems impossible to escape the conclusion that both the Werrie basalts and the interbedded and underlying sediments are equivalent in age to the Lower Marine Series of the Hunter Valley.

Triassic.

Only the basal portion of the Triassic system was examined. Three isolated outcrops occur and one of these in the north-west of the area has already been described (Hanlon, 1947). The other main outcrop is situated on a low hill between Borambil and Chilcott's creeks. A small outcrop, surrounded entirely by Tertiary basalt, occurs near the western boundary of the Parish of Temi, adjacent to the point where the Parish of Gregson adjoins the Warrah Estate.

The rocks examined consist of coarse conglomerates which are interbedded with fine conglomerates and sandstones. The coarse conglomerate is characterised by the presence of abundant jasper pebbles.

Tertiary.

Tertiary basalt and dolerite occupies quite a large proportion of the area mapped and occurs in the form of sills, dykes, flows and irregular intrusive masses. Two main centres of the igneous activity are located at Mt. Temi and Jack White's Mountain. Sills have been intruded in places between the Carboniferous and Permian rocks and at various levels in the basal portion of the Permian system.

Tertiary basalt occurs both above and below the basal portion of the Lower Willow Stage, which contains the oil-shale horizon adjacent to Mt. Temi. In the creek below the oil-shale mine, the Tertiary basalts can be seen intruding the Permian sediments. The basalts between the oil-shale horizon and the sediments at the Devil's Pinch probably consist of a sill or series of sills of Tertiary basalt intruded between the Werrie Basalts. In the time available during the course of the survey it was impossible to make any separation of the different basalts.

Flows of Tertiary basalt occur along the top and slopes of the Liverpool Ranges. The boundaries have not been traversed in detail and in many places are sketched. Isolated outcrops are found on the tops of many hills and along and adjacent to faults throughout the area.

Tertiary to Recent.

These deposits comprise the alluvium along Borambil and Chilcott's creeks. It consists of black sticky clay containing gravel beds and has been derived mainly from the weathering of the Werrie and Tertiary basalts. The gravel beds yield good supplies of underground water at shallow depths.

STRUCTURAL GEOLOGY.

The central portion of the area is made up of the Back Creek Dome and the elongated nose which forms the southern extension of the Castle Mount Dome. The latter is offset about two miles westerly from the northern nose of the Back Creek Dome. Together they form an anticlinal zone which trends west of north and has a core of Carboniferous rocks. The south-western limit of this zone is formed by Permian strata which are in turn overlain unconformably by the Triassic system (Hanlon, 1947). To the east lies the Temi Basin, so named because of its situation relative to Mt. Temi and the parish of the same name. It continues under the Liverpool Range and can be traced southwards until cut off by the Murrurundi thrust. Except for Tertiary basalt, the rocks outcropping in the basin belong entirely to the Lower and Werrie Stages of the Willow Series.

Several faults are shown on the Geological Map of the Willow Tree-Temi District (Plate VIII), and most of them are considered to be thrusts. Once the faults pass into the Werrie Basalts it is almost impossible to trace them for any great distance. The faulting may consist of a zone made up of a series of oblique thrusts arranged *en echelon*, in which case the faults in the north-west of the Temi Basin may die out southwards. If any of them continue they would probably pass immediately north of Jack White's Mountain, cross the Liverpool Range in the vicinity of Mt. Temi, and then continue through the Parish of Temi, County of Brisbane, north of the area to be described in Part III of the Geology of the North-Western Coalfield.

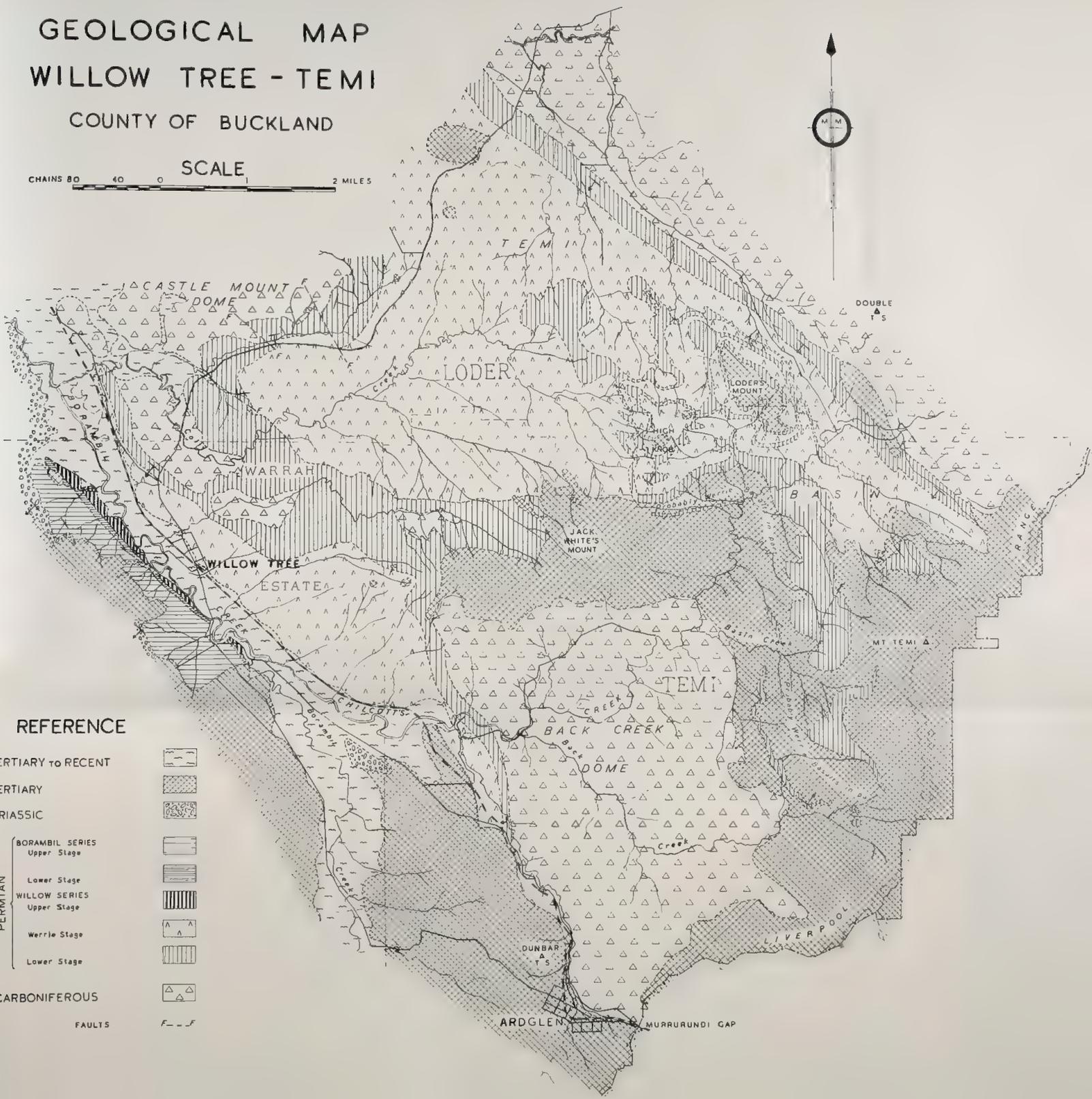
Where the area mapped joins the Werrie Basin the conclusions reached as to the structure differ somewhat from Carey's (1934) original interpretation. The Castle Mountain Dome is a fairly broad structure until its southern termination is reached. Here it narrows suddenly and its southern continuation is represented only by the relatively narrow nose referred to earlier. It is considered that the relief of the stresses developed during the folding was brought about by the formation of a series of thrusts, in some of which the movement was largely

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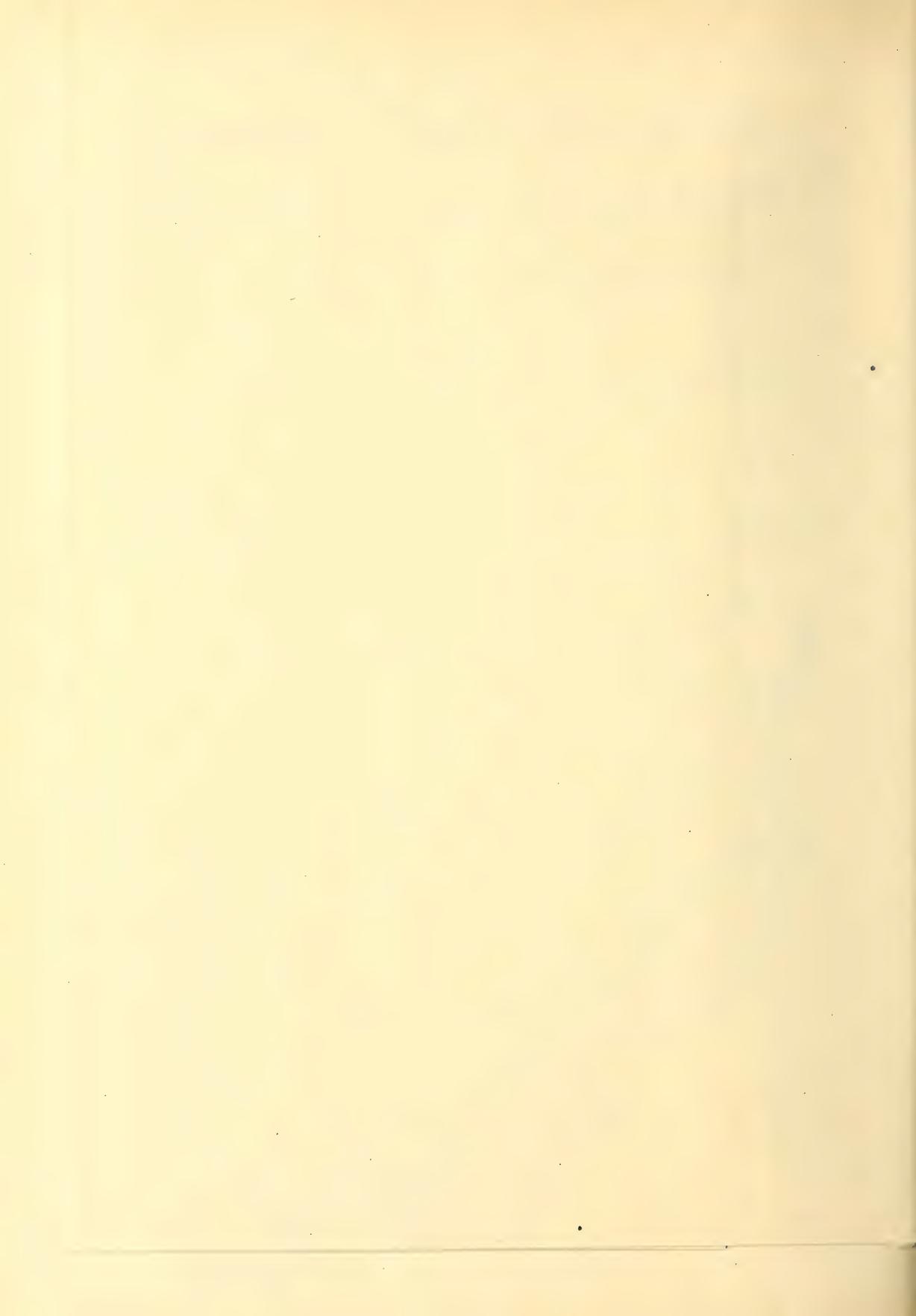
GEOLOGICAL MAP WILLOW TREE - TEMI COUNTY OF BUCKLAND

CHAINS 80 40 0 SCALE 2 MILES



REFERENCE

- TERTIARY TO RECENT
- TERTIARY
- TRIASSIC
- PERMIAN
 - BORAMBIL SERIES Upper Stage
 - Lower Stage
 - WILLOO SERIES Upper Stage
 - Werrrie Stage
 - Lower Stage
- CARBONIFEROUS
- FAULTS



horizontal, and that the present disposition of the strata can be explained in this way rather than by a series of later normal faults. (The Colly Creek faults of Carey.)

It is also considered that the Triassic shore line was not very far from the edge of the present Carboniferous hills along the Willow Tree-Quirindi Road, and that it is difficult to say to what extent the sudden change from the Carboniferous hills to the alluvial flats is due to faulting, and to what extent it is the result of shore line conditions, although it must have been caused partly by faulting.

The folding of the sediments and the thrust faulting are considered to be intimately related. The age of the folding has already been discussed (Hanlon, 1947). It only remains to add here that the local development in the Temi Basin of the higher bands of sediments belonging to the Lower Willow Stage shows that a synclinal structure commenced forming in the area as early as Lower Marine time. This development probably had considerable influence on the location of the Temi Basin during the main folding and faulting which took place in Late Permian time.

In the area between Mount Temi and Jack White's Mountain several faults were developed and would appear to be related to the intrusion of the igneous rocks during Tertiary time. Further movement along some of the thrust faults may also have taken place during the Tertiary period.

ACKNOWLEDGEMENTS.

I was assisted on the survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him are gratefully acknowledged. I am indebted to Mr. H. O. Fletcher, of the Australian Museum, for the determinations of the Lower Marine fossils. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

The area consists of Carboniferous, Permian and Triassic rocks which have been affected by intrusions and flows of Tertiary age. The Carboniferous forms the core of an anticlinal zone and the north-eastern flank of the Temi Basin, which is occupied by sediments and volcanics of Lower Marine age. The south-western flank of the anticlinal zone is occupied by Permian strata, which dip vertically in places and are overlain with an almost right-angled unconformity by the Triassic. It is considered that the degree of unconformity would lessen markedly in a south-westerly direction and the relationship between the Triassic and Permian would become conformable.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD.
PART III. GEOLOGY OF THE MURRURUNDI-TEMI DISTRICT.

By F. N. HANLON, B.Sc., Dip.Ed.
Geological Survey of New South Wales.

With Plate IX.

(Presented by permission of the Under Secretary for Mines.)

Manuscript received, November 19, 1947. Read December 3, 1947.

INTRODUCTION.

The area mapped adjoins the Willow Tree-Temi district (Hanlon, 1947b) along the Liverpool Range, and on the south the area mapped by Dr. H. G. Raggatt in the vicinity of Blandford and Wingen. The geology is shown on Plate IX. The boundaries on the eastern portion of the Parish of Murulla, County of Brisbane, between the Page's River and the railway line have been taken from unpublished maps by Dr. H. G. Raggatt.

The survey was in the nature of a reconnaissance and rocks not belonging to the Permian System were mapped only in so far as was necessary to determine the boundaries of the Permian, and the general structure of the area.

TOPOGRAPHY AND ACCESS.

The area is located in the County of Brisbane immediately south and east of the Liverpool Range and comprises parts of the Parishes of Isis, Murrurundi, Murulla, Temi and Timor. It is traversed by the New England Highway and the Main Northern Railway Line. Murrurundi is 219 miles and Blandford 215 miles from Sydney by rail. Access by road varies, although it is mostly fair. Some of the more mountainous sections are accessible only by horse or on foot.

Topographic relief is considerable. The lowest lying section of the district is adjacent to Blandford, which is less than 1,400 feet A.S.L., while the highest point is Mt. Temi, approximately 4,113 feet A.S.L. The positions of creeks, particularly small tributary creeks, shown on the parish maps are often inaccurate, and on the geological map to accompany this paper (Plate IX) the positions of some of them have been replotted.

Generally speaking the more elevated sections of the area are occupied by Tertiary igneous rocks or Carboniferous strata, the lower lying sections consisting of Permian beds.

GEOLOGY.

The rocks of the area comprise the following formations, which are described in detail below, commencing with the oldest :

Tertiary to Recent

Tertiary

Jurassic.

Triassic.

Permian

Upper Coal Measures

Upper Marine Series

Lower Coal Measures

Willow Series

{ Werrie Stage
Lower Stage

Carboniferous—

Upper Kuttung Series

Upper Glacial Stage.

Carboniferous.

The Carboniferous stratigraphy was not studied in any great detail. The strata belong to the Upper Glacial Stage of the Upper Kuttung and consist of fluvio-glacial conglomerates, varves, tuffs and acid lavas. The sudden lateral variation of the varves to conglomerates mentioned previously (Hanlon, 1947*b*) is shown very well along the lower part of Warland's Creek, where there are also excellent examples of contorted varves.

Permian.

The Murrurundi-Temi area forms a connecting link between the Permian strata of the Willow Tree district and the Upper Hunter. The Upper Coal Measures, Upper Marine Series and Lower Coal Measures are connected with beds of the same age, which have been mapped continuously from the south and the classification adopted in the type area has been retained for them. The Werrie and Lower Stages of the Willow Series are only partly connected by mapping with the Lower Marine of the Hunter Valley and the classification adopted in the Willow Tree area (Hanlon, 1947*a*) has been applied to them.

Willow Series. The Lower and Werrie Stages of the Willow Series are considered to be the equivalents of the Lower Marine of the type area in the Hunter Valley. However, only freshwater and no marine fossils were found in either stage in the Murrurundi-Temi district. The correlation has been discussed in detail previously (Hanlon, 1947*a*, 1947*b*). Although the strata below the Lower Coal Measures to the south of the area mapped have not been examined, descriptions of them suggest that a proportion of the uppermost beds which have been mapped as Carboniferous may belong to the Werrie and Lower Stages of the Willow Series.

Lower Stage. It consists of freshwater sediments comprising sandstones, shales, tuffs and carbonaceous beds and contains fragmentary plant remains. Mr. C. J. Ivin has collected *Gangamopteris cyclopteroides* from the Temporary Common in the Parish of Murulla and *Phyllothea australis* from the vicinity of portion 74, Parish of Temi. The formations mapped represent the basal sub-stage of the Willow Tree-Temi area (Hanlon, 1947*b*). Beds of tuffs, agglomerates and conglomerates are found interbedded with the Werrie Stage and would correspond to similar bands found on the northern side of the Liverpool Range. Time did not permit the individual boundaries to be traversed, and these bands have not been shown on the Geological Map of Murrurundi-Temi (Plate IX).

Sandstones which contain bands of oil-shale occur in the Parish of Temi to the north of the area mapped. They are considered to represent part of the Lower Willow Stage, which has been brought into its present position by faulting. The faulting is probably in part at least of Tertiary age and associated with the intrusion of Tertiary basalts and trachytes. Late Permian thrust faulting may also have affected the area.

Werrie Stage. It consists mainly of amygdaloidal basalts which weather rapidly and are always more or less decomposed. The lowest flows are interbedded with the upper beds of the Lower Willow Stage. In some places basalts similar to the typical Werrie Basalts occur below the base of the Lower Stage, between it and the Carboniferous. However, it is impossible to say whether they represent early flows or locally developed sills. They may even be Tertiary basalt sills.

Lower Coal Measures. They comprise shales, sandstones, grits and conglomerates with bands of concretionary ironstone and a coal seam. The nature of the sedimentation is essentially similar to that of the Upper Willow Stage of the Willow Tree district, although the total thickness of the sediments seems to be less than the probable thickness at Willow Tree, and the coal seam appears to be closer to the top of the series. The seam has been prospected adjacent to the Page's River on portion 65, Parish of Murulla, by means of an inclined shaft. South of the area mapped and north-east of Wingen township, the seam has been on fire for many years in the vicinity of Burning Mountain (David, 1907).

Upper Marine Series. It consists of conglomerates, sandstones and shales and has been mapped by Dr. H. G. Raggatt (unpublished) northwards from Wingen to the Page's River in the Parish of Murulla, where certain horizons contain an abundant marine fauna. The sediments continue across the Page's River and can be traced around the Sandy Creek syncline in the Parish of Isis. Near the boundary between the Parishes of Isis and Timor, a band of conglomerate near the base of the Upper Marine is overlain by shales containing abundant *Glossopteris* and plant remains and the resistant sandstone bands which are developed on the western limb of the syncline appear to be absent. It seems, therefore, that either the Upper Marine thins rapidly in this direction or else that marine give way to fresh water conditions. Northwards from Splitter's Creek the Upper Marine is not recognizable although adjacent to the Murrurundi Thrust there is a bed of conglomerate which may be the same as the conglomerate bed referred to above. However, in the absence of fossil evidence it is thought preferable not to map any Upper Marine but to show the Lower Coal Measures as grading out into the Upper Coal Measures.

Upper Coal Measures. The formations comprise conglomerates, in places very coarse, sandstones, shales and coal seams. The beds are mostly soft and easily eroded. In many places the beds closely resemble portions of the Upper Stage of the Borambil Series at Willow Tree. At some points the matrix of the conglomerates has weathered away to such an extent that the outcrops consist almost entirely of loose pebbles. Dr. H. G. Raggatt (unpublished) reported marine fossils above what was taken as the base of the measures.

Coal has been reported in many localities throughout the area, but the seams are mostly only one foot to 18 inches thick. The only exception is a thick seam which was struck in a well in portion 58, Parish of Murulla. It is probably dipping very steeply and is adjacent to the Murrurundi Thrust. The associated strata may represent a block of Lower Coal Measures which has been dragged up adjacent to the fault. However, in the absence of proof of a second fault in front of the Murrurundi Thrust, or the discovery of Upper Marine strata so

located as to explain the occurrence of Lower Coal Measures in this position, it is impossible to map the seam as belonging to any but the Upper Coal Measures.

Dips in the Upper Coal Measures vary from very steep to low. The upper beds are generally obscured by talus from the overlying Triassic conglomerates.

Triassic.

They consist of two stages, a lower conglomeratic stage and an upper sandy stage. The Lower Stage consists of conglomerates and sandstones and is characterized by abundant jasper pebbles in the conglomerates. Outcrops of bands of these conglomerates tend to form cliffs and make conspicuous physiographic features. The Upper Stage consists mainly of sandstones and shales, the latter being very lenticular. Good sections can be seen along the New England Highway between Murrurundi and the "Gap".

Jurassic.

A small outcrop of Jurassic shales occurs adjacent to the Great Northern Railway line to the south of the tunnel near Murrurundi Gap. Jurassic plants were discovered in these beds by Dulhunty (1939). They are very soft and form poor outcrops.

Tertiary.

Tertiary dolerites and basalts form widespread outcrops throughout the area mapped. They occur as flows, sills and dykes. Except for one small break at the Murrurundi Gap, the basalt is continuous along the crest of the Liverpool Range. Several isolated hills are capped by basalt.

At least one plug of trachytic composition occurs adjacent to the area mapped. Some of the outcrops of similar material within the Murrurundi-Temi district probably represent sills or dykes of Tertiary age. They occur within both the Carboniferous and Permian strata, but have not been mapped separately.

Tertiary to Recent.

These deposits are confined to the alluvium along the Page's River and its tributaries. The alluvium is derived from the coal measures and Carboniferous sediments as well as basalts. It is much lighter in colour and less clayey than that along Borambil Creek, north of the Liverpool Range, which is derived largely from the weathering of Werrie and Tertiary basalts.

STRUCTURAL GEOLOGY.

The area is divided into two portions by the Murrurundi Thrust. North of the thrust the structures represent the southerly continuation of the Back Creek Dome and Temi Basin which were obscured by Tertiary basalt along the top of the Liverpool Range. The formations exposed are similar, the core of the Back Creek Dome being composed entirely of Carboniferous rocks and the outcrops in the Temi Basin being confined to the Werrie and Lower Stages of the Willow Series, except for intrusions and flows of Tertiary age.

South of the Murrurundi Thrust the synclinal zone, of which the Temi Basin forms a part, is continued. It has been named the Sandy Creek Syncline from its relationship to the course of Sandy Creek. It is closed to the south, at least as low stratigraphically as the upper beds of the Werrie Stage, and the nose may have been affected slightly by faulting. The syncline pitches to the west of north and is flanked on the south-west by an anticline which pitches in conformity with it. The strata exposed are much higher stratigraphically than

those outcropping north of the Murrurundi Thrust and comprise portions of the Upper Coal Measures, Upper Marine Series, Lower Coal Measures and Werrie Stage, below which the mapping was not continued.

The relationship of the Triassic to the Permian is obscured by talus. However, although the Upper Coal Measures adjacent to the railway line dip steeply, there is no definite evidence of any unconformity between the two formations.

Numerous small faults occur in the area, particularly adjacent to the Murrurundi Thrust, but they have not been mapped because in most instances they are impossible to trace and can only be recognized at one point.

By far the most important fault in the area is the Murrurundi Thrust. It has a general east-west strike and has been traced from west of the Murrurundi Gap to the eastern edge of the area mapped and continues eastwards some distance beyond this point. It cannot be traced westwards because it passes beneath the Tertiary basalt. The isolated bar of steeply dipping Triassic sandstone in portion 63, Parish of Temi, referred to above, is almost on the continuation of the line of the fault. The northern side of the fault has moved upwards and westwards relative to the southern side. The amount of movement must have been considerable, because in the area immediately east of the Murrurundi Gap the Carboniferous strata is faulted so as to be above both the Triassic and Jurassic, which are dipping very steeply. This represents the complete elimination of the whole of the Permian system. If the thickness of the Permian here is comparable with that exposed at Willow Tree, it represents the elimination of well over 6,000 feet of strata without counting the thickness of Triassic and any Carboniferous beds which may be concealed. It is considered to be a thrust rather than a normal fault for the following reasons. Firstly, there is a northerly dipping fault zone on or adjacent to the line of the Murrurundi fault in portion 1*b*, Parish of Murrurundi. Secondly, there is a series of small thrust faults in the upthrown block adjacent to the main fault above Scott's Creek. From their relationship to the main fault they would be in the nature of underthrusts. Thirdly, the beds on the downthrow side of the fault have been dragged up until they are practically vertical. This applies without exception to the Jurassic, Triassic and Permian strata, and is considered to be more consistent with thrust than normal faulting.

The age of the folding and faulting have been discussed previously (Hanlon, 1947*a*, 1947*b*). The discussion will not be repeated except to draw attention to the outcrops of Triassic and Jurassic strata near Murrurundi Gap which have been dragged up along the fault until almost vertical and prove that at least some of the movement along it took place in post-Jurassic time.

ACKNOWLEDGEMENTS.

I was assisted on this survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. A. B. Walkom for the determination of the fossil plants collected by Mr. C. J. Ivin. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

I also wish to express my sincere thanks to Mr. C. J. Ivin, of Murrurundi, for information made available. Mr. Ivin is an amateur geologist who has made the geology of the Murrurundi district his hobby over a period of many years. His views coincide with the writer's in most instances. He recognized the synclinal areas which have been named by the writer, the Temi Basin and the Sandy Creek Syncline, and also traced the Murrurundi fault. He maintained the Werrie Basalts were of Lower Marine age, a contention which the writer has since proved correct. He also correlated the underlying freshwater sediments

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on the opposite sides of the Liverpool Range, but differed from the writer's views by placing them in the Carboniferous. The main point of difference between his and the writer's views was that he considered the Temi oil-shale deposit and similar deposits on the Murrurundi side of the Liverpool Range as being Tertiary. He has also carried out a considerable amount of work on the Carboniferous and Devonian strata east of the area under consideration. His work has not been published and the writer considered that some mention of it should be made.

SUMMARY.

The area is divided into two portions by an east-west thrust fault and comprises a synclinal zone trending west of north which is flanked on the west by an anticlinal zone. Outcrops consist of Carboniferous, Permian, Triassic and Jurassic strata, together with intrusions and flows of Tertiary igneous rocks. The main folding and faulting was probably late Permian in age, but further considerable movement took place along the thrust fault at least as late as Jurassic and possibly during Tertiary time.

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Obituary.

FREDERICK STAPLETON MANCE was born in Parramatta in 1872 and died in Sydney on August 24th, 1945. He was educated at Sydney High School and entered the Public Service (Department of Mines) in 1890. After a distinguished career he was appointed Under-Secretary for Mines in 1928. Mr. Mance took a very great interest in all public activities and was closely associated with any movement that had as its objective the education and enlightenment of the public, especially the younger people. He was President of the Board of Trustees of the Australian Museum and belonged to our Society for twenty-one years. He is survived by a wife, son and daughter.

RICHARD OLD, a life member, died at his home on July 24th, 1945. He had been a member of the Royal Society for forty-three years.

JOHN POWELL, who was born in London eighty-one years ago, died in Sydney on July 24th, 1945. His early life was spent in Kent at his father's country store. After a few months at sea he became connected with the grocery trade in Maidstone, Kent. Following a successful business career, he joined the staff of Messrs. Foster, Clark Limited. In 1917 the firm sent him to Australia to commence manufacture here. He was made Managing Director of Foster, Clark (Australia) Ltd., and a director of Messrs. Peek Frean (Aust.) Pty. Ltd.

He attended London University and worked in History and Economics. He was a pioneer of adult education in England and brought to this country many ideas of the London School of Economics. He was a Fellow of the Royal Economic Society of London.

ALLAN CLUMIES ROSS died in Sydney on February 10th, 1946, at the age of 57. He was born at Bathurst, N.S.W., and was educated at All Saints' College, Bathurst, Sydney High School and the University of Sydney, where he graduated in Science in 1910. After graduation he taught physics and mathematics at the Townsville Grammar School and the North Sydney Church of England Grammar School.

He served as a sergeant in the 17th battalion, A.I.F., in the 1914-18 war, was gassed in France, was subsequently commissioned and served in the Army Education Service in England until the middle of 1919. During this war Mr. Clumies Ross served in the Commonwealth Directorate of Man-Power, first as Assistant Director of Scientific Personnel and then, up to his death, as Controller of Scientific Personnel.

On returning to Australia from World War I he qualified as an accountant and became an authority on finance, taxation and business administration, being elected President of the Commonwealth Institute of Accountants. Mr. Clumies Ross retained his early interest in education and was for a number of years Lecturer in Business Principles and Practice in the Faculty of Economics, University of Sydney, and in advanced courses in Business Administration under the University Appointments Board. The width of his interests and activities was evidenced by his membership of the Economic Society of Australia and New Zealand and of the Royal Society of New South Wales, in both of which he served for a number of years as a member of Council and as an Honorary Treasurer; he was also a foundation member and councillor of the Industrial Management. In addition, he was the author of several books on business and accountancy matters.

Mr. Clumies Ross had been the Honorary Treasurer of our Society since 1941, and his high ideals and his devotion to duty, as well as his professional skill, were recognized by all of us who had the good fortune to come in contact with him.

THOMAS HODGE SMITH died in Sydney on June 8th, 1945, at the age of 51. He was born at Swindon, Wiltshire, England, and was brought to Australia at the early age of two. He was educated at Scots College, Sydney Technical High School, Sydney Technical College, and the University of Sydney. He served with distinction in the Royal Australian Navy in New Guinea during 1914 and 1915, and from 1916 to 1918 in France, where he was severely wounded. After his return to Australia he again took up his position with the Department of Mines as a Geological Cadet, and subsequently became Assistant to the Mineralogist. In 1921 he joined the staff of the Australian Museum as Mineralogist, and in 1941, became Officer-in-charge of Preparation, Australian Museum.

In the scientific world Thomas Hodge Smith will be remembered as a morphological crystallographer and as an authority on Australian meteorites. In his early years as mineralogist at the Museum, he carried out a good deal of field work, especially as regards the occurrence of zeolite minerals in New South Wales and on the mica fields of central Australia. From 1925 until the time of his death he was teacher of mineralogy at the Sydney Technical College.

His scientific interests, apart from his official duties, were numerous. He was a Fellow of the Australian and New Zealand Association for the Advancement of Science, and an active member of a number of other scientific societies, including the Royal Society of New South Wales which he joined in 1922. In recent years he was the Chairman of the Section of Geology.

EDWARD SUTHERLAND STOKES, who was born at Newcastle, N.S.W., died at the age of 76 on April 12th, 1945. He was educated at the Newcastle Grammar School and subsequently studied medicine at the University of Sydney. His medical career was most varied, and he became an outstanding authority in problems of public health, particularly on the chemistry and bacteriology of water and the treatment of sewage. During the first world war he served as a member of the Australian Medical Corps, going abroad in 1914, and after return from Gallipoli, in 1915, he was promoted to the rank of Colonel and appointed to the position of Principal Medical Officer of the Second Military District. In 1917 he returned to the Water and Sewerage Board, where he had been Medical Officer since 1904.

After his retirement from the Board in 1935 he practised privately as a water technologist until 1942, when, due to the exigencies of the war, he returned to his old post, from which he finally retired in December, 1943.

LESLIE VICKERY WATERHOUSE was born in Sydney in 1886 and died on November 27th, 1945. He was educated at the Sydney Grammar School and the University of Sydney, graduating B.E. in Mining and Metallurgy in 1910. His undergraduate course was interrupted by a twelve months travel abroad. He joined the Broken Hill Proprietary Company in 1910 as an assistant assayer, where he made special investigations into the newly introduced flotation process and its particular applicability to the treatment of low grade copper ores. In associating himself with various mining concerns, he soon became established as a very successful mining engineer and made his influence felt. For many years he took a prominent place in the Australasian Institute of Mining and Metallurgy, acting as one of the New South Wales representatives on the Council, and becoming President in 1938. He played a very prominent part in the development of gold mining in New Guinea, and as a director of Guinea Airways did important work in developing air transport of heavy machinery and merchandise. He was a member of the Royal Society of New South Wales for twenty-three years.

PROFESSOR JAMES THOMAS WILSON died at Cambridge at the great age of 84 on September 2nd, 1945. During his stay in Sydney, from 1887 to 1920, he played an outstanding role in the community as an educator and organizer, and was one of the founders of the medical school of the University of Sydney. At the early age of 29 he was appointed to the newly created Challis Chair of Anatomy, a position which he occupied till he was invited to the Professorship of Anatomy in the University of Cambridge. In recognition of his outstanding contributions in the realm of Anatomy, he was made an Honorary Member of our Society in 1922.

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

April 2nd, 1947.

The Annual Meeting, being the six hundred and thirty-ninth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Forty-three members and visitors were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

J. A. DULHUNTY, D.Sc.

Vice-Presidents :

R. L. ASTON, B.Sc., B.E. (*Syd.*), M.Sc.,
Ph.D. (*Camb.*), A.M.I.E. (*Aust.*).
F. LIONS, B.Sc., Ph.D., A.R.I.C.

H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

Hon. Secretaries :

D. P. MELLOR, D.Sc., F.A.C.I.

F. R. MORRISON, A.A.C.I., F.C.S.

Hon. Treasurer :

G. D. OSBORNE, D.Sc. (*Syd.*), Ph.D. (*Camb.*).

Members of Council :

R. C. L. BOSWORTH, M.Sc., D.Sc. (*Adel.*),
Ph.D. (*Camb.*), F.A.C.I., F.Inst.P.
R. O. CHALMERS, A.S.T.C.
H. O. FLETCHER.
F. N. HANLON, B.Sc.
W. H. MAZE, M.Sc.

R. S. NYHOLM, M.Sc.
D. J. K. O'CONNELL, S.J., M.Sc., F.R.A.S.
P. M. ROUNTREE, M.Sc. (*Melb.*),
Dip.Bact. (*Lond.*).
J. L. STILL, B.Sc., Ph.D.
O. U. VONWILLER, B.Sc., F.Inst.P.

The Annual Balance Sheet and Revenue Account were submitted to members. In the absence of the Honorary Treasurer, they were presented by Dr. D. P. Mellor, who moved the adoption. The motion was seconded by Dr. J. A. Dulhunty, and carried unanimously.

THE ROYAL SOCIETY OF NEW SOUTH WALES.
BALANCE SHEET AS AT 28th FEBRUARY, 1947.

LIABILITIES.

1946.		1947.
£		£ s. d.
246	Accrued Expenses	92 3 2
13	Subscriptions Paid in Advance	14 14 0
68	Life Members' Subscriptions—Amount carried forward	60 0 0
	Trust and Research Funds (detailed below)—	
1,875	Clarke Memorial	1,908 13 8
1,030	Walter Burfitt Prize	1,065 7 10
726	Liversidge Bequest	700 0 0
3,248	Research	3,322 8 4
		6,996 9 10
25,775	ACCUMULATED FUNDS	25,978 10 3
	Contingent Liability—In connection with perpetual leases granted to Australian National Research Council and the Pharmaceutical Society of N.S.W.—Maximum Liability £901 16s. 8d.	
(902)		
£32,981		£33,141 17 3

ASSETS.

1946.		1947.
£		£ s. d.
344	Cash at Bank and in Hand	292 8 3
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—	
	Held for—	
	Clarke Memorial Fund	1,800 0 0
	Walter Burfitt Prize Fund	1,000 0 0
	Liversidge Bequest	700 0 0
	Research Fund	3,000 0 0
	General Purposes	4,360 0 0
10,660		10,860 0 0
26	Prepayment	61 5 0
	Debtors for Subscriptions	97 14 0
	Deduct Reserve for Bad Debts	97 14 0
		—
14,715	Science House—One-third Capital Cost	14,715 0 0
6,800	Library—At Valuation	6,800 0 0
393	Furniture—At Cost—less Depreciation	373 0 0
32	Pictures—At Cost—less Depreciation	30 4 0
11	Lantern—At Cost—less Depreciation	10 0 0
£32,981		£33,141 17 3

TRUST AND RESEARCH FUNDS.

	Clarke Memorial.	Walter Burfitt Prize.	Liversidge Bequest.	Research.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Capital at 28th February, 1946 ..	1,800 0 0	1,000 0 0	700 0 0	3,000 0 0
Revenue—				
Balance at 28th February, 1946	75 2 5	30 12 10	25 15 0	247 15 0
Interest for twelve months ..	64 13 9	34 15 0	25 15 0	99 5 0
	<hr/>	<hr/>	<hr/>	<hr/>
<i>Deduct</i> Expenditure ..	139 16 2	65 7 10	51 10 0	347 0 0
	31 2 6	—	51 10 0	24 11 8
Balance at 28th February, 1947 ..	<hr/> £108 13 8	<hr/> £65 7 10	<hr/> —	<hr/> £322 8 4

ACCUMULATED FUNDS.

Balance at 28th February, 1946	£ s. d.
Add Surplus for twelve months (as shown by Income and Expenditure Account)	25,774 18 6
	<hr/>
	26,030 0 3
Less Increase in Reserve for Bad Debts	51 10 0
	<hr/>
	£25,978 10 3

G. D. OSBORNE,
Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1947, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 21st March, 1947.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1946, to 28th February, 1947.

1945-6.		1946-7.		
£		£	s. d.	£ s. d.
492	To Printing and Binding Journal—Vol. 79	355	8 7	
310	„ Salaries	363	0 0	
145	„ Library—Purchases and Binding	124	16 7	
49	„ Printing—General	68	1 0	
171	„ Miscellaneous	102	8 7	
63	„ Postage and Telegrams	95	2 1	
42	„ Rent—Science House Management Committee	42	14 8	
37	„ Cleaning	39	17 6	
23	„ Depreciation	22	9 0	
19	„ Telephone	18	14 9	
15	„ Insurance	15	4 3	
12	„ Audit	12	12 0	
9	„ Electricity	8	7 9	
1	„ Repairs	—		
<hr/>		<hr/>		
1,388				1,268 16 9
73	„ Surplus for Twelve Months			255 1 9
<hr/>		<hr/>		
£1,461				£1,523 18 6

1945-6.		1946-7.		
£		£	s. d.	£ s. d.
478	By Membership Subscriptions			521 17 0
400	„ Government Subsidy			400 0 0
425	„ Science House—Share of Surplus			436 0 0
131	„ Interest on General Investments			144 19 4
	„ Receipts from Reprints	65	2 0	
13	„ Less Expenditure	59	3 2	
		<hr/>		5 18 10
1	„ Other Receipts			1 1 0
13	„ Proportion of Life Members' Subscriptions			8 0 0
	„ Annual Dinner—			
	Received	57	14 0	
	Less Expenses	51	11 8	
		<hr/>		6 2 4
<hr/>		<hr/>		
£1,461				£1,523 18 6

The Annual Report of the Council (1946-47) was read, and on the recommendation of Dr. Bolliger, adopted.

REPORT OF THE COUNCIL, 1946-47 (RULE XXVI).

We regret to report the loss by death of three members since April 1st, 1946: Henry Gordon Farnsworth (1921), Sir George A. Julius (1911) and Carl Adolph Sussmilch (1901).

By resignation the Society has lost seven members: Jean Armytage, Una Black, Daphne Buckley, Ronald S. Clarke, E. A. Eastaugh, Arthur C. A. Flack and P. Hindmarsh.

The membership now stands at 314, 22 new members having been elected during the year, namely Gordon Alfred Barclay, Ernst Herbert Blaschke, Bruno Breyer, Keith Edward Bullen, Rodney Thomas Cook, Norma Winifred Donohoo, Felix Gutmann, Ernest John Jasper, Nora Hinder, Guy Frederick Johnson, Michael Lederer, John Charters McPherson, Helen May McRoberts, Albert May, Charles St. John Mulholland, Norman Pinwell, Bryce Harrison Potter, Cecil Rhodes-Smith, Beryl Scott, Ifor Morris Thomas, Margaret Crowley Weston and Norman Richard Wyndham.

Eleven ordinary meetings of the Council and two special meetings were held during the year commencing April 1st, 1946, at which the average attendance was 15. During the same period, nine general monthly meetings were held, the average attendance being 37.

Two special meetings of Council were held for the purpose of discussing the Society's objects. Many suggestions were made with a view to obtaining greater attendance at general meetings, and for a recognition of the Society's influence in the scientific world and in the community. It is expected that proposals arising from these discussions will be implemented in the near future.

Election of Councillor.—Miss Phyllis Rountree, B.Sc., Dip.Bact., was elected to the Council at the special Council meeting of August 7th, 1946, in place of Mr. P. Hindmarsh, who had resigned.

Twenty-two papers were accepted for reading and publication during the year, and the following short talks and lecturettes were given:

"Australian Gem Stones", by R. O. Chalmers, A.S.T.C.

"Synthetic Diamond", by D. P. Mellor, D.Sc., F.A.C.I.

"Some Recent Advances in Cellular Metabolism", by J. L. Still, M.Sc., Ph.D.

"New Instruments of Scientific Interest", by D. P. Mellor, D.Sc., F.A.C.I.

"Consciousness and Instinct", by A. S. Le Souef.

Film.—A film of the eruption of Ruapehu was screened.

Exhibit.—Exhibit and demonstration of the Geiger Counter was given by N. A. Faull, B.Sc., A.Inst.P.

Symposia.—At the monthly meeting of August 7th, 1946, a symposium on "Power Resources of the Commonwealth" was held, the following addresses being given:

"Fuel Energy", by J. A. Dulhunty, D.Sc.

"Solar Energy", by T. Iredale, D.Sc., F.R.I.C.

"Atomic Energy", by R. B. Makinson, B.Sc., Ph.D.

At the meeting of October 2nd, 1946, a second symposium was held, the subject being "Tracer Elements". The following addresses were given:

"The Production and Measurement of Radio-active Isotopes", by N. A. Faull, B.Sc., A.Inst.P.

"The Use of Radio-active Tracers in Biological Investigations", by W. P. Rogers, Ph.D.

Commemoration of Great Scientists.—The November meeting was devoted to the commemoration of great scientists, and the following addresses were given:

"Boucher de Perthes—The Antiquity of Human Culture", by Professor A. P. Elkin.

"Gottfried Wilhelm Leibnitz", by W. B. Smith-White, B.Sc.

"Tycho Brahe", by H. W. Wood, M.Sc.

"Valerius Cordus and the Pharmacopœia", by Dr. A. Albert.

Popular Science Lectures.—Five Popular Science Lectures were delivered in the months of May, July, August, September and October.

The lectures were much appreciated by members of the Society and the general public.

May 16th.—"Extinct Monsters", by H. O. Fletcher.

July 18th.—"A New Road for the Disabled Soldier", by Professor O'Neill.

August 15th.—"Recent Developments in Plastics", by A. R. Penfold, F.A.C.I., F.C.S.

September 19th.—"The Smallest Forms of Life—Virus", by P. M. Rountree, M.Sc., Dip.Bact.

October 17.—"Triumph over Pain—The Story of Anæsthesia", by Dr. W. I. T. Hotten.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1946 was delivered by Professor L. A. Cotton, M.A., D.Sc., on June 20th, 1946, the title being "The Pulse of the Pacific".

Clarke Memorial Medal.—The Clarke Memorial Medal was awarded to Mr. J. M. Black, A.L.S. (*honoris causa*), of Adelaide, in recognition of his distinguished contributions to natural science in Australia.

Liversidge Research Lectures.—The Liversidge Research Lectures were delivered by Dr. L. H. Briggs, D.Phil. (Oxon.), D.Sc. (N.Z.), at the Chemistry Department of the Sydney University on August 12th and 13th, 1946, the subject being "Plant Products of New Zealand".

Government Grant.—A grant of £400 was received from the Government of New South Wales. The Society greatly appreciates the Government's continued interest in its activities.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition. During 1946 £200 was invested in the Commonwealth Security Loan.

Royal Society, London.—Dr. Edgar Booth, of the International Wool Secretariat, and Mr. A. Maccoll represented the Royal Society of New South Wales at the commemoration celebrations in honour of Sir Isaac Newton, held in London, July, 1946.

Annual Dinner.—The Annual Dinner was held on March 27th, 1947, in the Withdrawing Room, Union Refectory, The University of Sydney. His Excellency Lieutenant-General John Northcott, C.B., M.V.O., Governor of New South Wales, and Miss Northcott were present, and the Minister for Education, the Honourable R. J. Heffron, represented the Premier and the State Parliament. A total of 81 members and friends were present. On this occasion the wives of guests were invited.

Science House.—The Royal Society's share of the profits in Science House during the period March 1st, 1946, to February 28th, 1947, was £436.

Science House Management Committee.—The Royal Society has had as its representatives at the meeting of the Management Committee of Science House Dr. G. D. Osborne and Mr. F. R. Morrison, and as substitute representatives Dr. J. A. Dulhunty and Mr. H. H. Thorne.

Pollock Memorial Fund.—On the recommendation of the Senate of the Sydney University the Council decided that the fund established in 1922 to perpetuate the memory of the late Professor J. A. Pollock, be placed in the Trust Fund of the University of Sydney. This Society is represented on the committee by the President, Mr. H. H. Thorne, Professor Vonwiller and the Honorary Secretary.

A.N.Z.A.A.S. Conference, Adelaide, August 20-27th, 1946.—Dr. A. Bolliger and Dr. G. D. Osborne were appointed as delegates to represent the Society.

Visit of the President to the United States of America.—Following the invitation to the President to nominate a representative of the Royal Society of New South Wales to attend the meetings of the National Academy of Sciences and the American Philosophical Society respectively, the President, Dr. F. Lions, was chosen by the Council to represent the Society. The meetings were held in Philadelphia and Washington from October 8th to 23rd, 1946.

During the absence of the President, Dr. A. Bolliger presided at meetings and undertook the duties of the President.

Sir Harold Spencer Jones.—The Astronomer Royal was welcomed by the Councils of the New South Wales Branch of the British Astronomical Association and the Royal Society of New South Wales, in the reception room of Science House, on Friday, February 21st, 1947, at 3.15 p.m. On the same evening, at 8 p.m., Sir Harold delivered a Popular Lecture entitled "Life on Other Worlds", in the Wallace Theatre, University of Sydney. The lecture was greatly appreciated by an audience of about 400 members of scientific societies and the general public.

Meeting of the Library Committee of Science House Owner Bodies.—The meeting was held on June 6th, 1946, to discuss the question of providing central library facilities for the owner bodies of Science House when building extensions envisaged had been effected. Although the three owner bodies were not in agreement regarding the merging of the separate libraries, unanimity was reached regarding provision of a common reading room.

The Library.—The amount of £38 19s. 1d. has been expended on the purchase of periodicals, and the amount of £82 17s. 6d. spent on binding; the total sum spent on the library over the past twelve months is therefore £121 16s. 7d.

Exchanges.—The number of volumes now being sent to other societies is 314.

Accessions.—For the twelve months ended February, 1947, the number of accessions entered in the catalogue was 2,177 parts of periodicals and 66 new books.

Borrowers and Readers.—Members and visitors reading in the library numbered 26.

The number of books and periodicals borrowed by members, institutions and accredited readers was 239.

Among the institutions which made use of the arrangements for inter-library borrowing were: Elliotts and Australian Drug Co., National Standards Laboratories, The Fisher Library, Sydney County Council, Australian Paper Manufacturers, Colonial Sugar Refining Co. Ltd., C.S.I.R., Canberra, Drug Houses of Australia, McMaster Laboratories, Siemens Australia Ltd., Amalgamated Wireless of Australia, Royal North Shore Hospital, Botanic Gardens and the Melbourne University.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member was read for the second time. The following person was duly elected a member of the Society: Raymond James Wood Le Fevre.

Election of Honorary Members.—The following were elected to honorary membership of the Society: Sir Harold Spencer Jones and Professor Frederick Wood Jones.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1947 to Dr. H. Lyman Clark.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1947 would be delivered by Professor H. S. Summers on July 17th.

Election of Auditors.—On the motion of Mr. R. S. Nyholm, seconded by Dr. J. L. Still, Messrs. Horley & Horley were re-elected as Auditors to the Society for 1947-48.

The retiring President, Dr. F. Lions, delivered his address entitled "The Freedom of Science".

At the conclusion of the address, Dr. Lions welcomed Dr. J. A. Dulhunty to the Presidential chair. The new President acknowledged the honour conferred upon him, and called upon Mr. Nyholm to propose a vote of thanks to the retiring President for his address and for his services to the Society during his term of office. This was carried by acclamation.

The following papers were read by title only: "The Orbit of H3494 ($2^h 15^m.6$, $-35^\circ 54'$: 1900)", by H. W. Wood, B.Sc.; "Note on the p-p'-Dinitro Diphenyl Disulphide", by G. K. Hughes and E. P. O'Leary; "Occultations Observed at Sydney Observatory during 1946", by W. H. Robertson, B.Sc.; "Dimensional Methods in the Design of Industrial Chemical Research", by R. C. L. Bosworth, Ph.D., D.Sc., F.A.C.I., F.Inst.P.; "Geology of the Ashford Coalfield", by F. N. Hanlon, B.Sc.; "A Magnetic Survey in the Vicinity of the Volcanic Neck at Dundas, N.S.W.", by F. N. Hanlon, B.Sc.

F. LIONS, President.

May 7th, 1947.

The six hundred and fortieth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Twenty-seven members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Lennard Robert Hall, James Charles Lloyd, William B. Smith-White.

Popular Science Lecture.—It was announced that the first Popular Science Lecture for 1947 would be given by Mr. W. H. Maze on Thursday, May 15th, at 8 p.m., and would be entitled "The Hunter River Valley—A Future T.V.A.?"

International Geological Congress.—It was also announced that the International Geological Congress would take place in London from August 25th to September 1st, 1948.

Library.—The following donations were received: 31 parts of periodicals and 77 back numbers.

Notice of Motion.—The President moved the following addition to the first paragraph of Rule V: "A copy of the list shall be posted to each financial member of the Society not less than ten days before the closing date for nominations."

The following papers were read:

"Studies in Semiquinones. Part I. p-Phenylenediamine and Benzidine Derivatives", by G. K. Hughes, B.Sc., and N. S. Hush.

"The Determination of Maximum Inherent Moisture in Coal by Controlled Vaporisation of Adherent Moisture", by J. A. Dulhunty, D.Sc.

The following paper was read by title only:

"A New Method of Approximating the Binomial and Hypergeometric Probabilities", by D. T. Sawkins, M.A. (Syd.), B.A. (Camb.).

The following papers read by title at the April general meeting were presented and discussed: "Dimensional Methods in the Design of Industrial Chemical Research", by R. C. L. Bosworth, Ph.D., D.Sc.

"Magnetic Survey in the Vicinity of the Volcanic Neck at Dundas, N.S.W.", by F. N. Hanlon, B.Sc., Dip.Ed.

Exhibit.—"Synthetic Minerals used in Optical and other Scientific Apparatus", by Miss F. M. Quodling, B.Sc.

Demonstration.—Dr. A. Bolliger gave a demonstration entitled "Some Photo-chemical Properties of Tungstic Acid".

June 4th, 1947.

The six hundred and forty-first General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Thirty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Charles Joseph Magee, Fritz Henry Reuter, Gregory Stewart Buchanan and Bruce Ritchie.

Popular Science Lecture.—It was announced that the second Popular Science Lecture for 1947 would be given by Mr. J. R. Kinghorn on Thursday, June 19th, at 8 p.m., and would be entitled "Snakes and Snake Venom".

Library.—The following accessions were received: 79 parts of periodicals and eight purchases.

Motion from Last Meeting.—The President moved the addition to the first paragraph of Rule V, notice of which had been given at the previous meeting, and announced that the proposed addition would be submitted for confirmation at the next general meeting.

The following papers were read:

"A Note on the Preparation of some o-Carboxy-Phenyl-Arsine Derivatives", by G. A. Barclay and R. S. Nyholm, M.Sc.

"The Colorimetric Estimation of Apomorphine", by E. R. Cole, B.Sc.

The following paper was read by title only:

"Theoretical Aspects of the Maximum Recovery in Absorption or Stripping Operation", by Geo. E. Mapstone.

Lecturette.—A lecturette entitled "Submarine Canyons, with special reference to recent discoveries off the South Australian Coast" was given by Dr. G. D. Osborne.

July 2nd, 1947.

The six hundred and forty-second General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Fifty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society: Ronald Louis Werner.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1947 would be delivered on Thursday, July 17th, at 8 p.m., by Professor H. S. Summers, and would be entitled "The Teachers of Geology in Australian Universities".

Library.—The following accessions were received: 218 parts of periodicals, three back numbers and 10 purchases.

Confirmation of Motion.—Addition to the first paragraph of Rule V. The President put the motion for its confirmation, which was carried.

The following papers were read:

"Possible Causes of Intraformational Disturbances in the Carboniferous Varve Rocks of Australia", by Rhodes W. Fairbridge, D.Sc., F.G.S. (Communicated by Professor L. A. Cotton.) Dr. G. D. Osborne contributed supplementary remarks on the paper.

"The Oxidation Potentials of the Tris 1, 10 Phenanthroline and Tris 2, 2' Dipyridyl Ferrous Ions", by F. P. Dwyer, D.Sc., and H. A. McKenzie, M.Sc.

"A Note on the Instability Constant of the Tris 2, 2' Dipyridyl Ferrous Ion", by F. P. Dwyer, D.Sc., and H. A. McKenzie, M.Sc.

Films.—The following films which had been made available through the good offices of Mr. R. S. Nyholm were screened:

1. "The Body Defences against Diseases."
2. "The Action of the Kidneys."
3. "Fuels and Heat."
4. "Light Waves and their Uses."

August 6th, 1947.

The six hundred and forty-third General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Twenty-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

Popular Science Lecture.—It was announced that the third Popular Science Lecture for 1947 would be given by Dr. R. L. Aston on Thursday, August 21st, at 8 p.m., and would be entitled "Measuring the Face of a Continent—the Use of Radar and Photography in Mapping".

Monographs.—The President also announced that an Editorial Sub-committee had been appointed with a view to publishing one or two monographs per annum.

Library.—The following accessions were received: 261 parts of periodicals, 13 purchases, 453 back numbers and two books.

The following papers were read :

"The Colorimetric Determination of Iron in Canned Foods with 1, 10 Pnenanthroline", by H. A. McKenzie, M.Sc.

"The Reaction of Pyridine with Dichlorotetrammine Cobalt (III) Complexes", by J. A. Friend and D. P. Mellor, D.Sc.

"A New Method for the Comparison of the Thermal Conductivities of Fluids. Part I", by R. C. L. Bosworth, Ph.D., D.Sc.

The following papers were read by title only :

"The Uniform Convergence of Sequences in Monotonic Functions", by F. A. Behrend, D.Sc.

"A Method of Determining the Distribution of Oil in a Reservoir Rock by Means of Ultra-Violet Light", by L. C. Noakes, B.A.

Lecturette.—A lecturette entitled "Some New American Research Tools" was given by Dr. F. Lions.

September 3rd, 1947.

The six hundred and forty-fourth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Thirty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Adrian Noel Old, Gladys Olive Conabere, Nancy Evelyn Ray and Reginald John Ray.

Popular Science Lecture.—It was announced that the fourth Popular Science Lecture for 1947 would be delivered by Mr. R. M. Gascoigne on Thursday, September 18th, at 8 p.m., and would be entitled "The Colouring Matter of Plants".

Library.—The following accessions were received: 102 parts of periodicals, 13 purchases, 40 back numbers and one book.

The following paper was read :

"Spectroscopic Characteristics of Ordinary Acheson Graphite", by K. B. Mather. (Communicated by Professor O. U. Vonwiller.)

The following papers were read by title only :

"The Petrology of the Silurian Volcanic Sequences at Wellington, N.S.W.", by M. J. Colditz, M.Sc.

"Studies in the Inheritance Resistance to Rust of Barley, I, II, III", by W. L. Waterhouse, M.C., D.Sc.

Discussion.—A discussion on Nuclear Science was held and the following short addresses were given :

"Stellar Energy", by H. W. Wood, M.Sc.

"Separation of Isotopes by Gaseous Diffusion", by R. C. L. Bosworth, Ph.D., D.Sc.

"Radioactive Tracers in Chemistry", by F. Lions, B.Sc., Ph.D.

October 1st, 1947.

The six hundred and forty-fifth General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Thirty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Alan M. Downes, Naida S. Gill, Stuart F. Gill, Leo Edmund Maley.

Popular Science Lecture.—It was announced that the fifth Popular Science Lecture for 1947 would be given by Dr. H. R. Poate on Thursday, October 16th, at 8 p.m., and would be entitled "The Story of Goitre".

Conversazione.—It was also announced that, following a letter received from the Emergency Committee of Atomic Scientists, U.S.A., signed by Albert Einstein, regarding Atomic Education, the Society would hold a *Conversazione* in the Great Hall, University of Sydney, on Wednesday, October 8th, at 8 p.m. Exhibits from the various departments of the University and the C.S.I.R. would be open for inspection, and would be followed by short addresses, which would be delivered by His Excellency the Governor of New South Wales, Lieut.-General John Northcott, C.B.,

M.V.O., the Minister for Education, the Honourable R. J. Heffron, the Chancellor of the University of Sydney, Sir Charles Bickerton Blackburn, and the Acting President of the Society, Dr. Francis Lions.

Library.—The following accessions were received : 179 parts of periodicals, four purchases and 115 back numbers.

The following papers were read :

“Corrosion of Surfaces Heated above the Boiling Point of the Corrodant”, by R. C. L. Bosworth, Ph.D., D.Sc.

“A New Method for the Comparison of the Thermal Conductivities of Fluids. Part II”, by R. C. L. Bosworth, Ph.D., D.Sc.

Lecturettes.—The following lecturettes were given :

“Palæontological Work in the U.S.A.”, by Dr. Ida Brown.

“Impressions of Chemical Research Activity in Britain”, by Dr. T. Iredale.

November 5th, 1947.

The six hundred and forty-sixth General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Forty-three members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of five candidates for admission as ordinary members of the Society were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Arthur S. Ritchie, Patrick R. McMahon, Peter Nordon.

Library.—The following accessions were received : 221 parts of periodicals, 204 back numbers and four purchases.

Sidey Summer-time Medal.—The Acting President, Dr. F. Lions, on behalf of the Royal Society of New Zealand, after a brief summary of the history of the award, presented the Sidey Summer-time Medal to Dr. D. F. Martyn, of the Commonwealth Observatory, Mount Stromlo, Canberra.

The award was made to Dr. Martyn for his work on radar and the reception of radio waves from the sun.

The following papers were read by title only :

“The General Geology of the Bombala District”, by H. M. McRoberts, B.Sc.

“The Geology of the Stanhope District, N.S.W.”, by B. Scott, B.Sc.

Commemoration of Great Scientists.—The meeting was devoted to the commemoration of great scientists, the following addresses being given :

(1) “Torricelli.”

“Helmholtz” : Enunciation of the Principle of the Conservation of Energy, by Mr. J. B. Thornton.

(2) “Simmelweiss” : Prevention of Puerperal Fever.

“Simpson” : Introduction of Chloroform Anæsthesia. (Illustrated with lantern slides), by Dr. K. Brown.

December 3rd, 1947.

The six hundred and forty-seventh General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Twenty-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of five candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Peter Beckmann, Neil E. Goldsworthy, Justin R. Humpoletz, George E. Mapstone, Gordon K. Webb.

Arnold Reymond Prize, 1951.—It was announced that a circular had been received from the University of Lausanne inviting applications for the award of the Arnold Reymond Prize, 1951.

Library.—The following accessions were received : 101 parts of periodicals, 209 back numbers and 10 purchases.

The following papers were read :

- “ The Chemistry of Bivalent and Trivalent Rhodium. Part X. The Oxidation of Cæsium Hexachloro-Rhodate (III) to Cæsium Hexachloro-Rhodate (IV) ”, by F. P. Dwyer, D.Sc., R. S. Nyholm, M.Sc., and L. E. Rogers, M.Sc.
- “ The Chemistry of Osmium. Part III. Complexes of Tertiary Arsines with Bivalent and Trivalent Osmium Halides ”, by F. P. Dwyer, D.Sc., R. S. Nyholm, M.Sc., and B. T. Tyson.
- “ Geology of the North-Western Coalfield, N.S.W. Part I. Geology of the Willow Tree District ”, by F. N. Hanlon, B.Sc.
- “ Geology of the North-Western Coalfield, N.S.W. Part II. Geology of the Willow Tree-Temi District ”, by F. N. Hanlon, B.Sc.
- “ Geology of the North-Western Coalfield, N.S.W. Part III. Geology of the Murrurundi-Temi District ”, by F. N. Hanlon, B.Sc.

Mr. Hanlon's papers were discussed by Dr. G. D. Osborne, who stated that the subject of the papers was very important from the viewpoint of (1) stratigraphy and (2) structural history at the end of the palæozoic era.

- “ The Colorimetric Estimation of Strychnine ”, by E. R. Cole, B.Sc.
-

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Mr. C. St. J. Mulholland.

Honorary Secretary : Mr. R. O. Chalmers.

Meetings.—Five meetings were held during the year, the average attendance being seven members and four visitors.

April 18th.—Address by Mr. L. Owen on "Some Aspects of Australian Coal". Exhibit by Mrs. K. M. Sherrard: *Corynoides* c.f. *calicularis*. This form is placed by Ruedemann among *formae incertae sedis*. It has not been recorded in Australia previously. It was found in black slates in the Shoalhaven Gorge near the mouth of Bungonia Creek and occurs with *Climacograptus bicornis* and its varieties, *Cryptograptus tricornis* and *Mastigograptus*.

June 20th.—Address by Dr. G. D. Osborne on "Evolution of the Structure and Physiography of the Sydney Basin".

September 19th.—Notes and Exhibits : By Miss Quodling : (a) Specimen of banded breccia from Hornsby ; (b) Specimen of gold in calcite from Hornsby. By Dr. Osborne : Andradite-wollastonite rock from the Oberon District. By Mr. Chalmers : Specimens of new minerals as yet undescribed, duplexite and bowleyite from Londonderry, near Coolgardie, Western Australia. Both are beryllium minerals. By Mr. Fletcher : A pseudo-fossil from Thudungara, N.S.W.

November 21st.—Meeting abandoned because of insufficient attendance.

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