A DICTIONARY

OF

APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

EMERITUS PROFESSOR OF GENERAL CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES OF THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, LONDON; LATE PRINCIPAL OF THE GOVERNMENT LABORATORY, AND A PAST PRESIDENT OF THE CHEMICAL SOCIETY AND OF THE SOCIETY OF CHEMICAL INDUSTRY

ASSISTED BY EMINENT CONTRIBUTORS

VOL. XI

REVISED AND ENLARGED EDITION

WITH ILLUSTRATIONS

1926

龍門聯合書局影印

1951

On the much-lamented death of Sir Edward Thorpe, on February 23, 1925, it was found that much progress had been made with the two last volumes of his Dictionary. The final revision for the press has been carried out by H. Forster Morley, M.A., D.Sc., F.I.C., who was joint Editor of the last edition of Watts's "Dictionary of Chemistry," and Director of the "International Catalogue of Scientific Literature." It is hoped that Vol. VII., containing an Index to the whole work, will be published before the end of 1926.

ABBREVIATIONS
OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Fis. Quim.	Anales de la Sociedad Española Física y Química.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim.	Annales de Chimie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik.	Annales der Physik.
Ann. Physique	Annales de Physique.
Ann. Report	Annual Reports of the Chemical Society.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth. Zeit.	Apotheker-Zeitung.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewer's Journal.
Brit. Assoc. Rep.	Report of the British Association for the Advancement of Science.
Brit. Med. J.	British Medical Journal.
Brit. Pat.	British Patent.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Asso. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim. Biol.	Bulletin de la Société de chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Umschau.	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
D. R. P.	Deutsches Reichs-Patent.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. Chim. Ital.	Gazzetta Chimica Italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Japan J. Phys.	Japanese Journal of Physics.

J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Bact.	Journal of Bacteriology.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
J. Chim. Phys.	Journal de Chimie Physique.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Met. & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
P.	Proceedings of the Chemical Society.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmaceutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. R. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitz.	Sitzungsberichte der K. Akademie zu Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Swiss Pat.	Swiss Patent.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
U.S. Pat.	United States Patent.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Z. Elektrochem.	Zeitschrift für Electrochemie.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. Kryst.	Zeitschrift für Kristallographie,
Z. Kryst. Min.	Zeitschrift für Kristallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Physik.	Zeitschrift für Physik.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

LIST OF CONTRIBUTORS

TO VOLUME VI.

HAROLD A. AUDEN, Esq., M.Sc. (Manchester), D.Sc. (Tübingen), *Research Chemist, Liverpool.* [SULPHURIC ACID.]

HARRY BAKER, Esq, F.I.C., *Chemist to the Castner-Kellner Alkali Co., Runcorn.* [SODIUM, pp. 155–195; 210–264.]

EDWARD CHARLES CYRIL BALY, C.B.E., M.Sc., F.R.S., F.I.C., *Grant Professor of Inorganic Chemistry in the University of Liverpool.* [SPECTROSCOPY.]

GEORGE BARGER, M.A., D.Sc., F.R.S., *Professor of Medical Chemistry in the University of Edinburgh.* [SAMANDARINE; SANGUINARINE; SANTONICA; SARSAPARILLA; SENECIFOLINE AND THE ALKALOIDS OF SENECIO SPP.; SENEGA ROOT; SENNA LEAVES; SNAKE VENOMS; SOLANINE; SQUILL; STROPHANTHUS; INSULIN; SYNTHETIC DRUGS.]

GEORGE STANFIELD BLAKE, Esq., A.R.S.M. [STRONTIUM.]

JOHN SAMUEL STRAFFORD BRAME, F.I.C., *Professor of Chemistry, Royal Naval College, Greenwich.* [SMOKE AND SMOKE PREVENTION.]

FRANCIS HOWARD CARR, Esq., C.B.E., F.I.C., *The British Drug Houses, Ltd.* [SCOPOLAMINE; STRAMONIUM.]

ALFRED CHASTON CHAPMAN, Esq., F.R.S., F.I.C., *Consulting, Analytical and Research Chemist.* [SPINACANE; SPINACENE.]

JAMES CONNAH, Esq., B.Sc., F.I.C., *late Deputy Government Chemist, Government Laboratory, London.* [SAKÉ; SOY; TEA.]

Sir HENRY DAVEY. [STEAM.]

WILLIAM PORTER DREAPER, O.B.E., F.I.C., *Consulting Chemist.* [SILK, ARTIFICIAL.]

J. J. FOX, Esq., O.B.E., D.Sc., F.I.C., *Government Laboratory, London.* [SULPHUR, MODIFICATIONS OF.]

ERNEST GOULDING, Esq., D.Sc., F.I.C., *Superintendent Scientific and Technical Department, Imperial Institute, London.* [SILK.]

Sir ALFRED DANIEL HALL, K.C.B., M.A., F.R.S., *Chief Scientific Adviser to the Board of Agriculture and Fisheries, London.* [SOILS.]

GEORGE GERALD HENDERSON, M.A., D.Sc., LL.D., F.R.S., F.I.C., *Regius Professor of Chemistry in the University of Glasgow.* [TERPENES.]

T. H. PERCY HERIOT, Esq., F.I.C., *Lecturer on Sugar Manufacture, Royal Technical College, Glasgow.* [SUGAR, pp. 427–447.]

GEORGE T. HOLLOWAY, Esq., A.R.C.S., F.I.C. (the late), *Metallurgical Chemist, London.* [TANTALUM.]

HERBERT INGLE, Esq., B.Sc., F.I.C., *late Chief Chemist to the Transvaal Agricultural Department.* [SAGO; SAINFOIN; SPINACH; STRAWBERRY, SUNFLOWER; TAPIOCA.]

JULIUS LEWKOWITSCH, Esq., M.A., Ph.D., F.I.C. (the late), *Consulting and Analytical Chemist, London.* Articles revised by C. AINSWORTH MITCHELL, Esq., M.A., F.I.C., *Secretary to the Society of Public Analysts, Editor of the "Analyst."* [SAFFLOWER OIL; SALMON OIL; SAPONIFICATION; SEAL OIL; SESAMÉ OIL; SEWAGE FATS; SOAP; TALLOW.]

ARTHUR ROBERT LING, M.Sc., F.I.C., *Professor of Brewing and of Biochemistry of Fermentation in the University of Birmingham,* and DINSHAW RATTONJI NANJI, D.Sc., F.I.C., *Lecturer on Brewing and Biochemistry of Fermentation in the University of Birmingham.* [STARCH; SUGAR ANALYSIS, pp. 447–484.]

GILBERT THOMAS MORGAN, O.B.E., D.Sc., F.R.S., F.I.C., *Professor of Chemistry in the University of Birmingham.* [SAMARIUM; SCANDIUM; SULPHIDE DYES; TERBIUM.]

ARTHUR GEORGE PERKIN, F.R.S., F.I.C., *Professor of Colour Chemistry and Dyeing in the University of Leeds.* [SAFFLOWER; SAFFRON; SANDERSWOOD; SAPONARIA OFFICINALIS; SCOPARIN; SCUTELLARIA ALTISSIMA; SOPHORA JAPONICA; SUMACH; TANNINS.]

JAMES CHARLES PHILIP, O.B.E., M.A., D.Sc., Ph.D., F.R.S., F.I.C., *Professor of Chemistry, Imperial College of Science and Technology, London.* [SOLUBILITY; SOLUTION; SPECIFIC GRAVITY.]

Sir THOMAS KIRKE ROSE, D.Sc., *Chemist and Assayer to the Royal Mint.* [SILVER.]

FREDERICK MAURICE ROWE, Esq., D.Sc., F.I.C., *Lecturer on Dyestuffs, College of Technology, Manchester,* assisted by J. S. H. DAVIES, Esq., B.A., Ph.D. [TETRAHYDRONAPHTHALENE.]

ALFRED GORDON SALAMON, Esq., F.I.C. (the late), *Analytical and Consulting Chemist, London.* [SULPHUR.]

FRANK SCUDDERS, Esq., F.I.C., *Consulting Chemist.* [SEWAGE.]

L. J. SPENCER, Esq., M.A., Sc.D., F.R.S., *Mineralogical Department, British Museum, London.* [SAL AMMONIAC; SAMARSKITE; SAMSONITE; SAND; SANDSTONE; SASSOLITE; SCAPOLITE; SCHEELITE; SCORODITE; SENARMONTITE; SERPENTINE; SHALE; SIDERITE; SILLIMANITE; SIPYLITE; SLATE; SMALTITE; SMITHSONITE; SODALITE; SPAR; SPENCERITE; SPERRYITE; SPHENE; SPINEL; SPODUMENE; STANNITE; STAUROLITE; STEENSTRUPINE; STEPHANITE; STIBIOTANTALITE; STIBNITE; STICHTITE; STOKESITE; STOLZITE; STROMEYERITE; STRONTIANITE; STRÜVERITE; STRUVITE; SULVANITE; SYENITE; SYLVANITE; SYLVITE; SYNGENITE; TALC; TANTALITE; TAPIOLITE; TARBUTTITE; TEALLITE; TETRADYMITE.]

JOHN I. WATTS, Esq., *Messrs. Brunner, Mond & Co., Ltd.* [SODIUM CHLORIDE.]

HILDA WALKER, M.B., Ch.B., *Lecturer in Physiology in the University of Birmingham.* [SUGAR IN BLOOD.]

Miss MARTHA A. WHITELEY, O.B.E., D.Sc., *Assistant Professor, Imperial College of Science and Technology.* [SERINE; TARTRONIC ACID; TAURINE.]

SYDNEY YOUNG, D.Sc., F.R.S., F.I.C., *Professor of Chemistry, Trinity College, Dublin.* [SUBLIMATION.]

1923, 56, 2086–2088; J. Soc. Chem. Ind. 1923, 42, 1204 A). It has also been proposed for use in quantitative analysis for the precipitation of various metals in place of sulphuretted hydrogen; lead, mercury, silver, copper, and cadmium are all quantitatively precipitable as sulphides, and chromic and aluminium salts are precipitated as hydroxides, by boiling their solutions with sodium thiosulphate (Faktar, Zeitsch. anal. Chem. 1900, 39, 345). For the reduction of silver thiosulphate by hyposulphite, *see* Steigmann (Kolloid. Zeitsch. 1920, 27, 249; Chem. Soc. Abstr. 1921, ii. 46, 147). For the compounds of silver thiosulphate and acetylene-silver acetylide, *see* Bhaduri (Zeitsch. anorg. Chem. 1913, 79, 355; Chem. Soc. Abstr. 1913, i. 241).

The preparation, testing, and application of various substances for the standardisation of thiosulphate solutions are described in detail, and their relative merits for the purpose discussed by Kolthoff (Pharm. Weekblad, 1919, 56, 644). The purest forms of potassium dichromate obtainable commercially contain free chromic acid or potassium chromate. A method for the detection and estimation of these is given, which depends on the location of a discontinuity in the conductivity curve on the addition of alkali or acid. If chromic acid is present the addition of standard alkali causes no increase in the conductivity of a dichromate solution until the free acid is neutralised. Similarly, no increase in conductivity is observed on the addition of acid to a solution containing chromate until all the latter has been converted into dichromate. For analytical purposes it is recommended to melt the pure dichromate in an electric furnace before use. The other substances examined are iodine, oxalic acid, cyanogen iodide, potassium iodate, and potassium bromate. All these are easily purified, and give results in the titration of thiosulphate with an error of less than 0·1 p.c. The greatest error, 0·07 p.c., was observed in titrating with dichromate (Chem. Soc. Abstr. 1920, ii. 49). *See also* Bertiaux (Chem. Soc. Abstr. 1920, ii. 554). According to Low (Chem. Soc. Abstr. 1921, ii. 133) the standard solution will keep almost indefinitely if stored in amber-glass bottles and treated with about 5 grms. of sodium hydroxide per litre to neutralise any carbonic acid present. It is standardised against the ordinary permanganate solution (the iron value $\times 1{\cdot}139$ = the copper value). About 35 c.c. of the permanganate solution are added to 150 c.c. of water, 5 c.c. of glacial acetic acid, and 6 c.c. of 50 p.c. potassium iodide solution, the liberated iodine is titrated with the thiosulphate solution until the colour is faint, starch and 2 c.c. of silver nitrate solution (about 4 grms. per litre) are added, and the titration is completed. The yellow colour of the silver iodide produced destroys the purple tinge of the mixture, and the delicacy of the end-point is thus enhanced. This method of standardisation is rapid and is recommended as being possibly more accurate than that based on the use of metallic copper. Rampsue and Pratt (Pharm. J. 1913, 91, 142) found that the strength of $N/2$ and $N/10$ sodium thiosulphate solutions remained stable after the solutions had been kept for eight months under varying conditions as to the exposure to light and the colour of the bottles in which they had been stored. In certain cases small quantities of sulphur separated but the decomposition was not of such a degree as to affect the titre of the solutions (Chem. Soc. Abstr. 1913, ii. 786). *See also* Kolthoff (Pharm. Weekblad, 1919, 56, 878; Chem. Soc. Abstr. 1919, ii. 341); Bohrisch (Pharm. Zeit. 1914, 59, 360; Chem. Soc. Abstr. 1914, ii. 482); Waterman (Chem. Weekblad, 1918, 15, 1098; Chem. Soc. Abstr. 1918, ii. 404).

Sodium thiosulphate is employed in the separation of iron and aluminium. A solution containing these two metals is treated in the cold with sodium thiosulphate; this gives rise to the aluminium thiosulphate, and when boiled it is decomposed, with evolution of sulphur dioxide and deposition of sulphur and alumina, while the iron salt is not further acted upon than to reduce all ferric salts to ferrous salts.

Sodium thiosulphate double salts.—Sodium thiosulphate forms a large number of double salts, many of which are of extremely complex composition. Those formed with copper and silver have been studied by Rosenheim and Steinhäuser (Zeitsch. anorg. Chem. 1900, 25, 72) and C. and J. Bhaduri (*ibid.* 1898, 17, 1). *See* also L. Shinn (J. Amer. Chem. Soc. 1904, 26, 947). Sodium stibio-thiosulphate, *see* Julius von Szilágyi (Zeitsch. anorg. Chem. 1920, 113, 69; Chem. Soc. Abstr. 1921, ii. 207).

Sodium thiosulphate and cupric nitrate in cold aqueous solution produce disodium tricuprous thiosulphate

$$3Cu_2S_2O_3,2Na_2S_2O_3,6H_2O$$

crystallising in yellow needles which, when well washed and air dried, are permanent. Other similar salts can also be prepared (Bassett and Durrant, Trans. Chem. Soc. 1923, 123, 1279).

Sodium thiosulphate, fused in its water of crystallisation, dissolves freshly prepared cuprous halides and cuprous thiocyanate, giving clear colourless aqueous solutions from which are obtained crystalline complex compounds unaffected by light (G. Canneri and R. Luchini, Gazz. chim. ital. 1922, 52, ii. 261). Sodium thoromolybdates, *see* Barbieri (Atti R. Accad. Lincei, 1913, [v.] 22, i. 781; Chem. Soc. Abstr. 1913, ii. 779).

Sodium trithiocarbonate Na_2CS_3,H_2O is obtained by adding the requisite amount of carbon disulphide to an alcoholic solution of sodium hydrosulphide or disulphide and adding ether when the thiocarbonate separates out. It forms deliquescent needles of a pinkish-yellow colour, and gives a reddish solution in water which is stable out of contact with oxygen or carbon dioxide. The *perthiocarbonate* $Na_2CS_4,3H_2O$, formed in the same way, crystallises in deliquescent brownish-yellow needles and gives a yellow aqueous solution. The heats of formation of sodium trithiocarbonate and sodium perthiocarbonate in alcoholic solution are, respectively, 5700 and 8550 cals. (Yeoman, Chem. Soc. Trans. 1921, 119, 38).

Sodium tungstate. For compounds of sodium with tungsten and tungsten derivatives, and the manufacture of sodium tungstate and its properties, *see* Art. TUNGSTEN, vol. vii. *See also* Smith (J. Amer. Chem. Soc. 1922, 44, 2027; Chem. Soc. Abstr. 1922, ii. 774). For the transformation points, *see* van Klooster and Germs (Zeitsch. anorg. Chem. 1914, 86, 369; Chem. Soc.

Abstr. 1914, ii. 460). For the equilibrium of sodium tungstate with sodium silicate and with potassium tungstate, *see* van Liempt (Zeitsch. anorg. Chem. 1922, 122, 175; Chem. Soc. Abstr. 1922, ii. 775). Specimens of sodium tungstate which are not alkaline to phenolphthalein contain complex tungstates. They may be suitable for use in Otto Folin's (J. Biol. Chem. 1922, 51, 419) system of blood analysis by addition of the requisite quantity of alkali (Chem. Soc. Abstr. 1922, ii. 596). For the preparation of sodium paratungstate, *see* Lottermoser (Kolloid Zeitsch. 1922, 30, 346; Chem. Soc. Abstr. 1922, ii. 510). For the action of sodium paratungstate in fusion on salts of the halogen acids and oxy-halogen acids, *see* Kuzirian (Amer. J. Sci. 1913, [v.] 36, 301; Chem. Soc. Abstr. 1913, ii. 865 and 872). The use of sodium paratungstate in the estimation of the metal in cyanides, *see* Kuzirian (J. Amer. Chem. Soc. 1917, 39, 2358; Chem. Soc. Abstr. 1918, ii. 82). Sodium oxalotungstite, *see* Collenberg (Chem. Soc. Abstr. 1920, ii. 115).

Sodium zincate. The solubility isotherm in the system Na_2O—ZnO—H_2O has been completely determined at 30° by dissolving zinc oxide in solutions of sodium hydroxide of various concentrations and determining the solubility. The following substances appear as stable, solid phases: zinc oxide, sodium zincate, $Na_2O,ZnO,4H_2O$, and the monohydrate of sodium hydroxide. Sodium zincate forms very strongly incongruent solutions; in solutions containing 1 part of sodium hydroxide to 2 parts of water, it is decomposed, with separation of zinc oxide. Amorphous, gelatinous zinc hydroxide is to be regarded as a phase of a varying water content; it is impossible to remove all adsorbed ions from it, and it is metastable as regards zinc hydroxide. In special circumstances zinc hydroxide may be obtained as a crystalline phase of the constant composition, $Zn(OH)_2$. This crystallised hydroxide is metastable at 30° with respect of zinc oxide (Goudriaan, Proc. K. Akad. Wetensch. Amsterdam, 1919, 22, 179; Chem. Soc. Abstr. 1920, ii. 113). *See* ZINC OXIDE, vol. vii.

H. B.

SOFT CEMENTS *v.* LUTES.

SOILS. (1) *Classification.*—Various classifications of soils have been proposed, the most general may be described as 'Genetic,' in which the position of the soil is determined by its origin, and the factors of climate and vegetation which have given rise to it. Tulaikoff (J. Agric. Sci. 1908, 3, 80) distinguishes:

1. Laterite soils developed in humid tropical climates and marked by a large proportion of hydrated ferric oxide and alumina.
2. Wind-blown loess soils.
3. Soils of the dry steppes, distinguished by their richness in soluble salts, often alkaline.
4. Black soils (Tchernozem), containing large quantities of neutral humus.
5. Gray forest soils, containing less humus, to which group most of the soils of Great Britain belong.
6. Peat and ashy soils (Podzol).
7. Tundra soils.

Under British conditions we may distinguish between sedentary soils which have arisen *in situ* through the weathering of the underlying rock, and drift soils (soils of transport or alluvial soils) which have reached their present position through the action of running water or ice. The mixed soils of steep slopes which have either been washed or rolled down from above and containing angular fragments of diverse origin are sometimes separated as colluvial soils.

The farmer is accustomed to classify soils according to the ease or otherwise with which they can be worked, as sand, loams, and clays, with suitable subdivisions, *e.g.* sandy loams. These terms possess, however, widely different meanings according to the amount of rainfall which prevails, and can only be given any scientific value by correlating them with the mechanical analysis of the soil.

(2) *Proximate composition of the soil: mechanical analysis.*—The texture of the soil and the manner in which it will behave under cultivation are determined by the relative proportions of sand, clay, calcium carbonate, and humus or organic matter which it contains. By sand is meant the coarser particles generally consisting of silica. As it is convenient to take an arbitrary limit of size, sand may be defined as consisting of particles smaller than 1 and coarser than 0·04 mm. in diameter. Such material is distinguished by the small amount of water it will contain and by its lack of coherence when dry. Clay consists of the finest particles present in the soil and is distinguished by the large amount of water that it will retain, by its plasticity and impermeability to water when wet, and by its power of shrinking and cracking when dry and swelling again on wetting. When diffused through water, the clay particles can be flocculated or coagulated by small quantities of various soluble salts (Comber, J. Agric. Sci. 1920, 10). The properties of clay may be regarded as due to the fact that the finer particles are either wholly colloidal or are coated with colloids on their surface. The rate of evaporation of water from a soil containing clay pursues a different course than the corresponding rate from sand, however fine (Keen, J. Agric. Sci. 1914, 6, 456; Trans. Faraday Soc. 1922, 17). Again, the absorption properties of a soil are explicable on the assumption that the clay particles are mainly colloidal. If we take 0·002 mm. as the superior limit of size for the clay particles they run down without any break to particles of ultra-microscopic size which remain indefinitely in suspension in a neutral liquid, forming a colloidal suspension. Regarded chemically clay is mainly a hydrated silicate of alumina (kaolinite), but the chemically active portions behave as if it were a zeolite, containing in addition to the alumina easily replaceable bases—potash, soda, lime and magnesia. In the clay fraction is also included a certain amount of very finely divided ferric hydrate and silica; these particles, however, do not behave as colloids. For the purposes of analysis, the clay particles are divided by their size and not by their chemical composition. It is generally convenient to distinguish the groups of particles intermediate between sand and clay as silts.

All fertile soils contain some proportion of calcium carbonate finely disseminated throughout the soil. The proportion may vary from 60 p.c. or more in purely calcareous soils down to an inappreciable amount. Soils in which

calcium carbonate and clay predominate are usually distinguished as marls.

The organic matter of soils consists in the main of the débris of previous vegetation. It is a mixture of various complex substances, some of them containing nitrogen, and from it a few distinct compounds have been isolated (*see* Schreiner, U.S. Bureau of Soils, Bull. 53 and 74). In fertile soils the organic matter usually possesses a neutral reaction and consists largely of calcium salts of the so-called 'humic acid.' Humic acid does not possess any distinct composition and though it may in part be identical with the humic acid that can be prepared by the decomposition of sugar, it cannot be obtained from soil in a state free from nitrogen. Humic acid is soluble in ammonia and other alkalis and may be extracted from soil, peat, &c., by first treating the material with hydrochloric acid to decompose the calcium humate, washing, and then extracting with an alkali solution from which it may be precipitated by acid (Beckley, J. Agric. Sci. 1921, 11, 66). Soils in which the organic matter predominates are always black in colour, retentive of water and possessed of a very friable texture when dry. These peaty or boggy soils may be either acid in reaction, *e.g.* peaty and moorland soils, or neutral like the soils of the Fens.

The separation of the soil into its proximate constituents is known as a mechanical analysis, and the process consists in grading the particles (*a*) according to the velocity of the stream of water by which they can be carried, or (*b*) according to the time in which they will remain suspended in a column of water of a given height. The two methods are identical in principle and may be made to give similar results, but in most laboratories it is convenient to adopt the beaker method of separation by suspension.

A. *Sampling.*—In Great Britain, the layer down to a depth of 9 ins. is usually considered to represent the soil. Probably a depth of 20 cms. would have been more satisfactory, since it represents more nearly the layer which is usually stirred by the plough, but so many analyses have now been made on the 9-in. basis that it is desirable to retain the convention. In certain cases of very shallow soils the soil changes suddenly at a smaller depth than 9 ins. into something which can hardly be regarded as sub-soil, as for instance, into pure chalk rock. In these cases, the sampling must be stopped at the line of division, which should be recorded. To obtain a sample two methods are commonly employed. In the first, a steel box, 6 ins. in section, is driven into the ground to a depth of 9 ins. and its contents removed. In the second case, an auger of not more than 2 ins. in diameter is employed. It is always necessary to take a number of samples on the same piece of land and mix them before analysis, and the advantage of the auger method lies in the number of samples that can be quickly obtained without unduly increasing the bulk of material to be handled. The first sampling is usually followed by a second one, taking the second 9 ins. to represent the subsoil. Small samples for examination, and even for approximate analyses, may be rapidly obtained down to a considerable depth by means of an auger such as is used by shipwrights. For details of sampling, Hall's 'The Soil' (Murray, 1920), p. 53, may be consulted.

The samples, on reaching the laboratory should be spread out on shallow trays to dry at a temperature not exceeding 40°. The process is much accelerated by occasionally stirring and by crumbling down the lumps of the stiffer soils with the fingers before they become quite dry. The dried soil is passed through a brass sieve with holes 3 mm. in diameter, the lumps being gently worked down in a mortar with a wooden pestle. The material passing through the sieve is approximately weighed and also the material remaining on the sieve, which is then thoroughly washed on the sieve under a stream of running water. After drying, the stones which remain on the sieve are weighed to obtain the proportion of stones in the total sample as brought from the field. The material which passes the 3 mm. sieve is regarded as the fine earth for analysis.

B. *Mechanical analysis.*—Two portions of 10 grms. and one of 50 grms. of the fine earth are weighed out. One 10-grm. portion is dried for 24 hours at 100°, and then heated in an open basin over an Argand at a dull red heat with occasional stirring to obtain (1) hygroscopic moisture, (2) loss on ignition. The second 10-grm. lot is placed in a basin and covered with 100 c.c. of *N*/5 hydrochloric acid to dissolve out the carbonates and break up the calcium humate. The soil is rubbed up into a fine paste with a rubber pestle made by fixing a small solid rubber bung on a stout glass rod. After standing for an hour the soil is thrown upon a tared filter and washed until all acid is removed. The filter and its contents are then dried, the loss representing the hygroscopic moisture *plus* soluble salts. The soil is now washed off the filter with water containing about 1 c.c. of ammonia in 500 c.c. water on to a small sieve made with No. 100 brass wire cloth, the portion passing through being collected in a beaker 7 or 8 c.c. in diameter with a mark on the side 8·5 c.c. from the bottom. The material on the sieve is dried and weighed to represent the coarse sand and fine gravel. As the proportion of this coarse material is likely to be affected by irregular sampling when determined on 10 grms. only, it is advisable to repeat these operations on the 50-grm. sample without, however, preserving the material passing through the sieve. The residue after drying and weighing is then divided into 'fine gravel' and 'coarse sand' by means of a sieve with round holes 1 mm. in diameter. The beaker containing the portion of the 10-grm. sample which passed through the wire cloth sieve is now well stirred with the rubber pestle, filled to the 8·5 mark with ammoniacal water and put aside to stand for 24 hours. The turbid supernatant liquid is then rapidly poured off into a large jar, and the deposit at the bottom of the beaker is rubbed up with a rubber pestle and more ammoniacal water as before. The operations of filling up to the mark, standing for 24 hours, and pouring off the turbid liquid are gone through as before and repeated every day as long as any material remains in suspension or the 24-hour period. Generally, 7 to 10 decantations will be sufficient, after which the bulk of turbid liquid is evaporated down and finally brought into a tared basin,

dried and weighed. This fraction consists of clay particles less than 0·002 mm. in diameter, together with a certain amount of humus. After drying it is heated as before and re-weighed to obtain the weight of the 'clay.' The sediment from which the clay has been removed is worked up as before in the beaker, which, however, is only filled to the depth of 7·5 cms. The contents are allowed to stand for 12 minutes only, when the liquid is poured off into a large jar as before. The operations are repeated until all the sediment settles in 12½ minutes and the liquid above is left quite clear. The contents of the second jar are now evaporated to dryness and weighed as in operation 3, before and after ignition; this fraction is designated 'fine silt' and consists of particles between 0·010 and 0·002 mm. in diameter.

The sediment remaining in the beaker is worked up afresh just as in the previous operations, the mark being now placed 10 cms. from the bottom of the beaker, and the time of settlement fixed at one hundred seconds. The sediment is dried and weighed as 'fine sand' while the portion that is poured off is obtained by evaporation as in the previous operations and is designated as 'silt.' The soil has thus been divided into the following series—

	Diameter in millimetres Max.	Min.	
1. Stones and gravel	—	3·0	Separated by sifting.
2. Fine gravel	3·0	1·0	
3. Coarse sand	1·0	0·2	
4. Fine sand	0·2	0·04	Separated by subsidence.
5. Silt	0·04	0·01	
6. Fine silt	0·01	0·002	
7. Clay	0·002	—	

The sizes of the particles in the above groups, which is determined by the depth of the liquid and the time of settlement, are purely conventional and are those in use by agreement in the United Kingdom. A more rapid method is described by Robinson (J. Agric. Sci. 1922, 12, 207).

Chemical Analysis.

As in a mechanical analysis, certain conventions as to the sampling, nature of the solvent, and time of its action have to be adopted. The conventions followed below are general in the United Kingdom. The air-dried fine earth passing the 3-mm. sieve is taken and a portion of about 100 grms. is ground in a mill or broken in a steel mortar until it all passes through a sieve with round holes 1 mm. in diameter. Hygroscopic moisture and loss on heating are determined as before.

For modifications of soil dried in the air, *see* Lebediantzer (Compt. rend. 1924, 178, 960; Chem. Soc. Abstr. 1924, i. 820).

C. Nitrogen is determined in 10 to 20 grms. of the ground material by Kjeldahl's process; no correction need be made for the nitrate that is present.

D. The determination of calcium and other earthy carbonates is of great importance, especially when the amount is low. It is not sufficient to determine the calcium, which may be present in considerable amounts as silicate, humate, &c., even when the soil is acid from lack of calcium carbonate. The earthy carbonates are best determined from the carbon dioxide evolved on treatment with acid, being calculated as though they consisted entirely of calcium carbonate. The most exact method, when the quantity involved is small, consists in liberating the carbon dioxide by treatment with dilute hydrochloric or phosphoric acid at room temperatures in a partial vacuum, free from carbon dioxide, air being afterwards drawn through the mixture in order to wash out the last traces of carbon dioxide. The carbon dioxide may be absorbed in dilute caustic soda and determined by double titration, or by baryta solution (*see* Hutchinson and MacLennan, J. Agric. Sci. 1914, 6, 324). The lime requirements of the soil are best determined by estimating the calcium withdrawn by the soil on shaking with a solution of calcium bicarbonate (*see* Hutchinson and MacLennan, J. Agric. Sci. 1914, 6; Chem. Soc. Abstr. 1914, ii. 784). *See also* Sanyel (Chem. Soc. Abstr. 1924, i. 820).

E. For the determinations of soluble constituents, 20 grms. of the powdered soil are placed in a flask of Jena glass, covered with about 70 c.c. of strong hydrochloric acid, and boiled for a short time over a naked flame to bring the acid to constant strength containing about 20·2 p.c. of pure hydrogen chloride. The flask is loosely stoppered, placed on the water-bath, and the contents allowed to digest for 48 hours. The solution is then cooled, diluted, and filtered. The washed residue is dried and weighed as the material insoluble in acids.

The solution is made up to a litre and aliquot portions are taken for the various determinations. The analytical operations are carried out in the usual manner, but special care must be taken to free the solution from silica and organic matter.

For determination of the potash and phosphoric acid, 50 c.c. of the solution is taken and evaporated to dryness, about half a gram of calcium carbonate being added during evaporation if the soil is poor in calcium. The contents of the dish are then heated over an Argand or a Bunsen burner at a black or very dull red heat, the material being constantly stirred with a small glass pestle made by flattening out the end of a glass rod. After cooling, a few c.c. of water is added and the mass is worked up with the pestle, 50–80 c.c. of water is then added and the contents of the dish are boiled for half an hour. The solution is filtered off, the residue washed and the solution taken for determination of the potash by precipitation with platinic chloride or perchloric acid in the usual way. The residue is washed back on to the dish, 50 c.c. of water and 10 c.c. of strong sulphuric acid are added and the whole boiled for half an hour. The solution is filtered and used for the determination of phosphoric acid by precipitation with ammonium molybdate, the molybdic acid precipitate being either weighed or estimated by titration. In some cases, finely divided ferric oxide comes through the filter paper in making up the solution, in which case 5 c.c. of hydrochloric acid is added and the whole evaporated nearly to dryness. This will bring the iron into solution, when it will not interfere with the determination.

Calcium, magnesium, iron, manganese, and sulphuric acid may also be determined in the hydrochloric acid extract.

The determinations just described give what is commonly called the total plant food in the soil. It will be seen that the quantities revealed are usually very great, if we consider that the layer of soil down to the depth of 9 ins. over an acre weighs from 2½ to 3 million pounds. As a rule, hydrochloric acid will extract something in the order of 0·1 p.c. of phosphoric acid and from 0·3 to 0·5 p.c. of potash, proportions which would correspond to about 3000 pounds of phosphoric acid and 10,000 lbs. of potash per acre, whereas the average crop will remove not more than 50 lbs. of phosphoric acid and 200 lbs. per acre of potash. It is clear that the quantities thus determined throw very little light upon the need, or otherwise, for the application of particular fertilisers to the soil, since the soil is shown to contain far more than is sufficient for a maximum crop. Even the extraction with hydrochloric acid does not measure the total amount of plant food in the soil; if, for example, the soil is completely brought into solution by fusion with ammonium fluoride as much as 2 p.c. of potash may be found in clay soils, and this quantity is in a sense the only absolute measurement that can be made.

In order to obtain by analysis some practical guidance as to the requirements of the soil, attempts have been made to discriminate between the total amount of plant food in the soil and that which may be regarded as readily available to the plant, *i.e.* that which is soluble in such weak solvents as may be at work under natural conditions. In the soil *in situ* there is every reason to suppose that the solvent action is carried on by water containing carbon dioxide in solution, partly by the natural soil water, and partly by the more concentrated solution of carbon dioxide which forms in contact with the plant roots that are always excreting carbon dioxide. As the gases entangled in the soil always contain more carbon dioxide than ordinary air (up to 5 p.c. by volume), the soil water contains a corresponding amount of carbon dioxide, and so becomes a more effective solvent of phosphoric acid and potash. Attempts have been made to use water saturated with carbon dioxide as an analytical agent to determine the available mineral constituents in the soil; but although this is the solvent with the best *à priori* justification, its use has not been general and there are not sufficient data obtained by its means for comparison. For the present, therefore, it must remain as a research method hardly available for general analytical purposes. It is customary to employ a solution containing 1 p.c. of citric acid to determine the phosphoric acid and potash that may be regarded as available. Other weak acids have been proposed, but none of them bring about any absolute discrimination between two distinct classes of material, one of which can be regarded as available for the plant, the other as dormant. All acids, when of equivalent strength, begin by dissolving the same amount of, *e.g.* phosphoric, acid from the soil in question. Reabsorption, however, immediately begins and the final equilibrium that is brought about, is conditioned by the soil materials and the nature of the acid used. Other available constituents which may be taken to measure the fertility of a given soil are the nitrates and the ammonium compounds and also the humus compounds soluble in dilute alkali—the soluble humus or *matière noire*—which represents that part of the organic matter in the soil likely to be readily oxidised.

F. *Nitrates.*—The soil sample must be rapidly dried in the steam oven, since slow drying at temperatures a little above the normal would result in the formation of nitrates. After drying the soil is roughly powdered and passed through a 3-mm. sieve as before. 200 grms. of the sample are then packed on a Buchner funnel, 6 ins. in diameter, connected with a filter pump. The soil is washed with successive portions of hot water, and if care is taken to avoid plastering the wet soil it is possible to wash all the nitrates through in the first 100 c.c. or so of the water that reaches the filtering flask. The nitrates in the solution thus obtained are estimated by the standard methods. In the Rothamsted laboratory, it has been found most convenient to proceed by reducing them to ammonia by the zinc-copper couple, as devised by Thorpe (Chem. Soc. Trans. 1873, 26, 541). Strips of thin sheet zinc about 6 ins. long and 1½ ins. broad are cleansed by immersion in dilute caustic soda, followed by very dilute sulphuric acid, and are then dipped in a dilute solution of copper sulphate until they have obtained a heavy black deposit of copper. After washing finally in ammonia-free water they are placed in a bottle with the soil extract and a crystal of oxalic acid. The bottle is kept in a warm place or an incubator at 25° for 24 hours, then the ammonia is distilled off and determined by titration or by 'Nesslerising.'

Full details of a simple procedure for accurately determining nitrates in soils by the phenoldisulphonic acid method are given by H. J. Harper (Ind. Eng. Chem. 1924, 16, 180). Perfectly clear and colourless soil extracts are obtained by using as decolorising agent copper hydroxide precipitated in the soil suspension from copper sulphate and calcium hydroxide. Experiments show that this substance removes inappreciable quantities of nitrate from the solution by adsorption, whereas animal charcoal adsorbs appreciable quantities of nitrate. The losses of nitrate which are due to the evaporation of acid filtrates, to the presence of chlorides in excess of 15 parts per million in the soil, and to the presence of carbonates in the residue to which the phenoldisulphonic acid is added, can be prevented by keeping the solution alkaline on evaporation, by removing the chlorides with silver sulphate, and by flooding the dry residue with 3 c.c. of phenoldisulphonic acid. Interfering tints that occur in making comparisons between standard solutions and those of unknown nitrate content are caused by the presence of organic colouring matter, by irregularities in the method of adding the different reagents, and by the presence of insoluble matter in the solution. They can be avoided by removing the organic matter with copper hydroxide, by treating all residues uniformly according to the procedure given, and by filtering to remove material not in solution (J. Soc. Chem. Ind. 1924, 43, B. 268).

For a comparison of various methods of determining nitrates in soil, *see* D. J. R. Van Wijk (Sol. Sc. 1924, 17, 163; Chem. Soc. Abstr. 1924, 126, ii. 566).

G. For determinations of the ammonium salts, 100 grms. of the soil are placed in a distillation flask with 2 grms. of magnesia and 100 c.c. of water. The tube from the flask is connected to a 100 c.c. pipette which leads into a filter flask serving as a receiver and containing 50 c.c. of standard acid. The distilling flask is placed in a water-bath kept at 30° and the filter flask is connected with a pump to maintain a partial vacuum. Distillation at this temperature proceeds for 6 hours, after which the pipette is disconnected and the acid titrated (*see* Russell, J. Agric. Sci. 1910, 3, 233).

H. *Available phosphoric acid and potash.*—200 grms. of air-dried soil are placed in a Winchester quart bottle with 20 grms. of citric acid and 2 litres of water. By the original method (*see* Dyer, Chem. Soc. Trans. 1894, 65, 115) the contents of the bottles are shaken from time to time for 7 days and then filtered; but it has been shown that identical results can be obtained in 24 hours if the bottle is placed in an end-over-end shaker and kept in continuous agitation. After filtering, two portions, each of 500 c.c., are taken for the determination of phosphoric acid and potash by the methods previously described, after evaporation and incineration to get rid of the citric acid and dissolved silica.

I. *Soluble humus.*—10 grms. of the air-dried soil are treated with dilute hydrochloric acid in order to decompose the humus as in the method for mechanical analysis. After filtering and washing away the acid the soil is washed into a flask with 500 c.c. of 4 p.c. solution of ammonia. Flask and soil are then shaken for 24 hours, allowed to stand for several hours, and filtered until 200 c.c. of filtrate are obtained. This, representing 4 grms. of the original soil, is then evaporated to dryness in a tared basin and weighed. The basin and its contents are heated to determine the ash and inorganic matter also present, the weight of which must be deducted from the weight of soluble humus previously obtained.

J. *Soil reaction.*—A determination of the acidity or alkalinity of the soil is of great importance towards estimating its fertility. The hydrogen ion concentration varies from a p-concentration of 10 to 3, a fertile arable soil shows about 8, soils at either extreme being sterile. Litmus and the other indicators are of little value in the determination, soil being so well buffered. For methods, *see* Fisher (J. Agric. Sci. 1921, 11, 1).

K. *Physical determinations.*—In addition to the mechanical analysis of soils, several other physical constants of soil have, from time to time, been determined: for example, the maximum and minimum water capacity, the capillarity, the apparent and real density, the hygroscopic moisture, the heat evolved on wetting (Benetzung-wärme), specific heat, &c. The methods by which these determinations are made may be found in standard works on soil, but at the present time little value can be attached to the results. Most of the figures obtainable, *e.g.* hygroscopic moisture, wilting coefficient, represent particular states of equilibrium not breaks in the smooth curve showing the relations of the soil to water. In many cases, the results are conditioned by the state into which the soil has been brought by the process of sampling, and as no satisfactory method exists of testing the soil *in situ* or bringing it in an unchanged condition into the laboratory, determinations made upon the usual samples possess no value. Further, in nearly all cases it is difficult to attach any interpretation to the results, *i.e.* to correlate them with the behaviour of the soil in the field (Hardy, J. Agric. Sci. 1923, 13, 340). To two determinations, however, some practical value may be attached, viz. the hygroscopic moisture and the water content when the soil is in the optimum working condition and possesses a crumb structure. Hygroscopic moisture is usually determined by exposing the dried soil in a shallow tray to an atmosphere saturated with moisture at the ordinary room temperature. The dish containing the soil is placed under a bell jar over water and the interior of the bell jar is lined with filter paper which dips into the water below. It will be found almost impossible to obtain consistent results by this method because of the deposition of dew upon the dish or the soil. A better method is to place the soil in a shallow layer in a flat boat contained in a wide tube. The tube is immersed in a water-bath, maintained at a constant temperature of 25° by a thermostat, and a slow current of air is drawn over the soil, the air current being previously bubbled through a potash bulb containing water immersed in the same bath, so as to become saturated with vapour at the temperature of the experiment. Consistent and comparable results can in this way be obtained, and the hygroscopic moisture thus determined serves as a measure of the absorbing surface possessed by the soil. The water content of the soil in its optimum working condition is a conception introduced by F. K. Cameron (J. Phys. Chem. 1910, 14, 320) and represents that condition in which the soil can be cultivated and made to break down into small particles without puddling. Several pounds of the soil in a dried condition are placed in a large basin and slowly wetted with a fine spray of distilled water; the soil is carefully worked about with the hands to equalise the wetting, and it will be found that a point is eventually reached when the soil is distinctly moist and yet can be broken down to a crumb without getting into a pasty condition. If the moisture is increased beyond this point, the soil becomes obviously wet and gets sticky and puddled when any attempt to work it is made. The experimenter must use his judgment as to when the right point has been reached, then a sample of the soil is taken and its water content determined. With a little practice it will be found that successive results can be obtained with the same soil that agree within 1 or 2 p.c. The mean of several determinations may be taken as the optimum water content.

For further particulars, the following books may be consulted: Hall, The Soil, London, 1920; Hilgard, Soils, New York, 1906; Wiley, Principles and Practice of Agricultural Analysis, vol. i.; Ramann, Bodenkunde, Berlin, 1911.

Bacteria of the Soil.

A recognition of the importance of the biological factors at work in the soil is comparatively recent, indeed it can hardly be said

to date further back than 1877, when Schloesing and Müntz showed that the formation of nitrates from the organic nitrogen compounds in the soil is a process brought about by a living agency. It is now agreed that as regards all the compounds of carbon and nitrogen present in the soil, their transformation into compounds capable of serving as food for plants is brought about by micro-organisms of one class and another, and that the fertility of the soil is very largely determined by the relative activity of the different groups. It is possible to show by the ordinary methods of plate culture that the soil contains bacteria in numbers of the order of 0·5 to 50 millions per gram of soil, and there are several important groups of bacteria which do not grow on the usual gelatine media and therefore do not get included in this account. In addition to the bacteria, the soil possesses a micro-flora of yeasts, moulds, and other fungi, while latterly certain higher organisms—protozoa and amœbæ, nematodes and the like, have been shown to play an important part in determining the activity of the lower organisms and therefore the fertility of the soil. A large amount of work has been done in the way of isolating and describing particular organisms present in the soil, but for practical purposes it is less important to identify species than to ascertain the collective activity of groups of organisms which possess the same function. Many efforts have been made to measure the activity of these various groups so as to obtain a quantitative estimate of the factors which determine the preparation or destruction of plant foods, but it cannot be said as yet that the methods devised are satisfactory, or have received general acceptance as leading to results which can be correlated with the fertility of the soil when determined by the yield of test plots.

The soil bacteria may be conveniently grouped under the following heads:—

(*a*) Humus-making organisms which transform carbohydrates and other plant residues into humus.

(*b*) Nitrogen-fixing organisms which are capable of taking up free gaseous nitrogen and bringing it into combination in the material of which their own cells are composed.

(*c*) Ammonia-making organisms which attack the proteins and other less complex compounds of nitrogen and break them down with formation of ammonia.

(*d*) Nitrifying organisms which oxidise ammonium compounds and give rise to nitrites and nitrates.

(*e*) Denitrifying organisms which reduce nitrates to nitrites and to free nitrogen gas. In this group are generally included a further set of organisms, probably distinct, which set free nitrogen gas from organic compounds of nitrogen.

In addition to these main groups there are other organisms which sometimes play an important part in the soil, for example, the reducing organisms which form sulphides, hydrogen sulphide, and free sulphur from sulphates, and the iron organisms which secrete hydrated ferric oxide from solutions containing ferrous carbonate.

1. The relative predominance of organisms of the bacterial or fungoid type seems to be determined by the reaction of the soil. In neutral or very slightly alkaline soils, bacteria predominate; in acid soils, micro-fungi are chiefly active; and many important groups of bacteria, such as those bringing about nitrogen fixation and nitrification, may be entirely absent.

For the determinations of the number of organisms present in the soil, and indeed for all determinations of bacterial action, special samples must be taken.

A thin brass tube about 1 in. in diameter, sharpened at the lower end like a cork borer, is forced into the soil to a depth of 6 ins., then placed in a sterilised glass tube plugged with cotton wool for removal to the laboratory.

Another method which is more convenient, as yielding samples from various depths, begins by the construction of a special boring tool which can be driven into the ground. The tool consists of two strips of steel, ¼ in. in thickness, 8 ins. long and 2 ins. wide, each bent down the whole length of the strip so as to form two wings, 1 in. wide, at right angles to one another. The edges are then bevelled off until the two pieces of steel can be put together so as to form a box, 1 sq. in. in section and 8 ins. long, in which position the pieces are retained by steel rings which can be forced over the two ends. The lower end of the tool is sharpened and it is then driven into the soil to the required depth of 6 ins. After removal, the rings can be knocked off, whereupon the box falls apart showing a square core of soil, any portion of which can be taken. In the laboratory the soil, still in a moist condition, is carefully broken down with a spatula and is worked through a sieve with holes 3 mm. in diameter. Two portions of 25 grms. are weighed out, one is dried to determine the water content, the other is shaken up for about 5 minutes with 250 c.c. of sterile physiological salt solution, containing 0·5 p.c. sodium chloride and 0·2 p.c. of magnesium sulphate. From this turbid liquid, 1 c.c. is pipetted off and added to another flask containing 99 c.c. of similar sterile salt solution. After well shaking 1 c.c. from this dilution is again transferred to a further 99 c.c. of sterile salt solution, and after again shaking 1 c.c. of this last dilution is added to a test tube containing 10 c.c. of nutrient gelatine, and the plate poured in the usual way. The plates are incubated for 8 days at a temperature of 20°; each plate represents ·0001 gram of soil in its moist state. The gelatin medium usually employed contains 1 p.c. of beef extract, 1 p.c. of peptone, and 0·5 p.c. of sodium chloride with 10 to 12 p.c. of gelatin. A gelatin medium has the advantage of showing the liquefying organisms, of which a separate count can be made; humus-making organisms can also be distinguished by the furry appearance of the colonies or even by the formation of a brown ring, but the gelatin has the disadvantage of inhibiting a number of organisms which do not develop in the presence of much organic nitrogen. In place of the gelatin, 1·5 p.c. agar may be used; but though the agar plates permit of the growth of other organisms, they do not distinguish between liquefying and non-liquefying organisms, and many motile organisms work about the surface and may obscure the results or give rise to secondary colonies. Another

useful medium is soil-extract agar made up as follows: Equal quantities of water and soil are boiled for half an hour and filtered, the liquid being further filtered through a Chamberland filter to get a clear extract. To the extract, 1 p.c. peptone and 1 p.c. dextrose or 1 p.c. dextrose alone are added, and the jelly is made up with 1½ p.c. agar as usual. This medium, without peptone, will permit of the growth of the nitrogen-fixing organisms, though it will inhibit the putrefactive, ammonia-splitting, and other organisms dependent upon combined nitrogen.

Another method of determining the collective action of the bacteria of the soil has been devised by Russell (J. Agric. Sci. 1905, 1, 261). He determines directly the oxidising power of the soil and finds it correlated with its fertility. The apparatus consists of a bulb of about 100 c.c. capacity with two tubes sealed into its neck, one of which is a long narrow tube dipping into mercury and constituting a gauge, while the other expands into a small flask partly filled at the beginning of the experiment with a solution of potash. 10 grms. of air-dried soil are placed in the flask with 2 c.c. of water, the flask is then sealed up and placed in a water-bath maintained at a constant temperature of about 20°. The apparatus is left for several days, whereupon the oxygen contained in the enclosed air is slowly converted into carbon dioxide which is absorbed by the potash, resulting in the diminution of the pressure of the enclosed air. Finally, the rate of oxidation is determined by the reduction in pressure which has taken place. It is necessary to make comparative trials with soils whose behaviour in the field is known, and while no absolute value can be given to the results, they are valuable as measuring the gross rate of bacterial activity in the soil and as supplying valuable indications of its fertility.

2. *Humus-making organisms.*—The decay of organic matter in the soil seems to proceed in two distinct fashions; in the presence of air the organic matter is broken down by micro-organisms of all kinds with the eventual production of carbon dioxide, water and ash. On the other hand, if the decay takes place under conditions which exclude oxygen, the process is more limited; carbon dioxide, marsh gas, hydrogen and other compounds are produced and there is left behind a black material containing more carbon but less oxgyen and hydrogen than the original vegetable matter. Both aerobic and the anaerobic decay gives rise to brown or black humus compounds, but it is not certain whether the same organisms take part in both processes or which predominate under ordinary soil conditions of partial exclusion of oxygen. The anaerobic processes have been studied in some detail, and Omelianski has isolated two organisms which are capable of attacking carbohydrates like cellulose. In one case, the products are carbon dioxide, hydrogen, various organic acids, and humus; and the other, which is perhaps the more general, carbon dioxide, methane, butyric and other organic acids, are produced. The process may be readily illustrated by filling a flask with a nutrient solution containing 0·1 p.c. KH_2PO_4, 0·1 $(NH_4)_2PO_4$, 0·05 $MgSO_4$, and a trace of NaCl, and introducing strips of filter paper with a small quantity of soil, or better still of pond mud. The flask is closed with an exit tube dipping down into water. After some days' incubation at 34°–35°, the filter paper will begin to disintegrate, at the same time gas will be given off consisting of a mixture of carbon dioxide, nitrogen, methane, and sometimes hydrogen. An aerobic organism which presumably plays the more important part in ordinary soil conditions has recently been isolated and investigated by Hutchinson and Clayton (J. Agric. Sci. 1919, 9, 143). This organism (*Spirochæta cytophaga*) exists in two forms, as a sinuous filamentous cell, feebly motile, and a spherical sporoid. The organism does not grow on ordinary gelatine or agar preparations, and does not utilise other carbohydrates than cellulose, indeed is inhibited by them. Its nitrogen requirements may be met by any of the simpler nitrogen compounds—ammonium salts, nitrates, &c. From the cellulose are produced a yellow pigment, small quantities of volatile acids, a mucilage which does not give rise to optically active compounds on hydrolysis, but no gas. Humus may be either acid (as in peat soils), or neutral when it is formed in the presence of calcium carbonate, as is usual in soils.

Nitrogen-fixing organisms.—The first demonstration that the soil contains bacteria capable of bringing gaseous nitrogen into combination was due to Hellriegel and Wilfarth in 1886, who showed that the small nodules which may be found upon the roots of clover, beans, and other leguminous plants contain colonies of bacteria living symbiotically with their host plant, deriving from it the carbon compounds which they need, and handing over nitrogen which they have 'fixed' from the atmosphere with which the plant roots are in contact. It was found that clover and other plants possessing such nodules upon their root do become richer in nitrogen and that in practice the soil is markedly enriched by their growth. Such gains in nitrogen only take place when the seedling plant can become infected either by growing in soil which normally contains the organism, or by addition to a sterile soil of either the extract from a nodule of some infected plant or a trace of normal soil. To the organism the name of *Pseudomonas radicicola* has been given, and further investigation has shown that while only one general species can be distinguished it has, to a certain extent, been specialised by association with particular plants. Thus better results are obtained when beans are inoculated with the organism derived from a nodule of a bean plant than with organisms from a lupin plant, and in some cases (lupins and lucerne) this specialisation has proceeded so far that the plant is only very slightly infected by the neutral form of the organism which exists in ordinary soil. In the soil, the organism appears to exist in minute rod-shaped organisms in rapid motion which infect the plant by passing through the cell walls of the root hairs. Inside the plant, the organism first of all develops into much larger rod-shaped organisms, which finally become, in the nodules, characteristically bent or Y-shaped organisms known as bacteroids. It is possible to cultivate *Pseudomonas radicicola* on the non-nitrogenous media described above, as, for example, soil-extract dextrose, agar-agar,

but the fixation of nitrogen under these conditions is inconsiderable.

From time to time, soils are found, the commonest example being peats and heaths of an acid reaction, in which *Pseudomonas radicicola* is not present, and when these soils are brought into cultivation, leguminous plants do not at first develop nodules and fix nitrogen. In this case, it may be desirable to proceed to an inoculation of the soil which, however, must first be rendered a suitable medium for the development of the organisms by the removal of its acidity and the addition of lime and phosphates. One method of effecting the inoculation is to strew over the field about ¼ ton to the acre of soil taken from a cultivated field on which the leguminous plants have been growing normally. Another method is to prepare an active culture of organisms from a nodule of the crop it is desired to sow, and with this prepare a large bulk of sub-culture by introducing it into ordinary tap water in which $\frac{1}{10}$ p.c. of dextrose and $\frac{1}{1000}$ p.c. potassium phosphate have been dissolved. Into the large bulk of crude culture thus obtained after standing two or three days, the seed, tied up in a thin muslin bag, is dipped and allowed to dry somewhat before sowing, when it will be found to carry with it sufficient organisms to ensure inoculation. As a rule, the leguminous crop still grows rather indifferently after its first inoculation, and only really flourishes when grown for a second or third time after the organism has established itself in the soil. Many attempts have been made to improve the growth of leguminous crops in ordinary soil by inoculating them before sowing, but, except in the special cases just mentioned, no success has attended the process. Amongst ordinary farm crops, the only call for inoculation appears to occur with lucerne when attempts are made to grow this plant on soils which have not hitherto carried it, since lucerne does not seem to be readily infected by the neutral form of organism, such as that left by the clover which may have been regularly grown on the same soil previously. Since the discovery of *Pseudomonas radicicola*, other organisms have been discovered living free in the soil which are capable of bringing nitrogen gas into combination. Winogradsky isolated from pond mud and other similar material under anaerobic conditions a widely diffused organism called *Clostridium pastorianum* which breaks down carbohydrates with the formation of humus, butyric acid, &c., accompanied by the fixation of a small amount of nitrogen—two to three mgm. for each gram of carbohydrate destroyed. The most important of the nitrogen-fixing organisms, however, is one discovered by Beijerinck, named by him *Azotobacter chroococcum*, which as such or as one of its closely allied forms has been isolated from soils in nearly all parts of the world. Its presence can be readily determined by adding a small portion of soil to 50 c.c. of sterile culture fluid containing per litre 10 grms. of mannite or glucose, 0·2 grm. each of potassium phosphate, magnesium sulphate, and sodium chloride, and 0·1 grm. of calcium sulphate and a trace of ferrous sulphate. The solution is placed in a small Erlenmeyer flask, ½ grm. of calcium carbonate added, the flask is plugged and its contents sterilised. After adding the soil the flask is placed in an incubator at 25° for a week, by which time a considerable fermentation will be found to have taken place accompanied by the evolution of carbon dioxide and the formation of a brown scum upon the surface of the liquid. *Azotobacter* is a powerful oxidising organism, converting the carbohydrate into carbon dioxide and water, together with small quantities of lactic and acetic acid, alcohol and sometimes butyric acid. At the same time about 9 to 10 mgs. of nitrogen are fixed for each grm. of carbohydrate oxidised. *Azotobacter* is a large oval organism, 4 to 5 μ in length and 3 μ in width. It differs from most bacteria in containing glycogen, so that it stains a deep brown colour with a solution of iodine. *Azotobacter* is not found on acid soils, the presence of calcium carbonate is essential to its development; to it and kindred organisms must be attributed a large share of the formation and maintenance of the stock of nitrogen contained in soils. Particularly to this agency do we look to explain the formation of the deep black soils of the Russian Steppes, the American North-West, Argentina, &c. It is, however, essential that the organism shall receive a supply of carbohydrate, by the oxidation of which it obtains the energy required to bring gaseous nitrogen into combination. At Rothamsted, it has been shown that the soil of the wheat field, from which the whole crop with the exception of a small quantity of roots and stubble is removed, gains very little nitrogen by bacterial agency, although the *Azotobacter* is present in the soil. An adjoining piece of land, however, on which the débris of grass and other wild vegetation fall back to the soil and is not harvested, there have been accumulations of nitrogen at a rate approaching 100 lbs. per acre per annum over a period of 25 years, and this case is parallel to the formation of the virgin soils above mentioned.

3. *The ammonia-making organisms.*—As a group the ammonia-making organisms have not received much study, although recently it has been shown that the fertility of the soil must be largely determined by their activity. The greater number of the organisms found in the soil—the organisms, for example, which grow upon gelatin plates including such well-known putrefactive organisms as *Proteus vulgare*, *Bacillus mycoides*, *B. mesentericus vulgatus*, *B. subtilis*, *Bact. fluorescens liquefaciens*, *B. coli*, &c., must belong to this group. Their general function is well known; they are capable of attacking proteins and resolving them successively into a lower form of combination, amino-acids, &c., until at last the nitrogen reaches the state of ammonia. In addition the soil contains other organisms not capable of dealing with the proteins, but resolving the simpler nitrogen compounds into ammonia. Of these the best known are the urea-splitting organisms, *Micrococcus ureæ*, *Urobacillus pasteurii* and *Planosarcine ureæ*, which hydrolise urea with formation of ammonium carbonate and water. These organisms which are exceedingly abundant in stables, cow stalls, &c., are also present in the soil. The dependence of the fertility of the soil upon the numbers of the ammonia-making organisms has been made evident by the work

of Russell and Hutchinson (J. Agric. Sci. 1909, 3, 111) on the effects of partially sterilising soil by heat or by exposure to the vapour of antiseptics like chloroform, toluene, &c. These investigators found that a soil which had been heated to a temperature of 100° for 2 hours and then placed under normal conditions favourable to growth gave rise to a much increased crop, the yield being in many cases doubled, while the amount of nitrogen in the plant became three or four times as great as that on the untreated soil. This increased crop was found to follow to a large extent the rate of the formation of ammonia in the soil, the ammonia in this case being taken up as such by the plant, because the nitrifying organisms had been destroyed. It was also found that the soil was not completely sterilised by the processes; the spores of certain groups resist the heat and develop to an unprecedented extent when the soil was once more placed under conditions favourable for growth. For example, a normal soil is found to contain about 8 million bacteria per gram before being subjected to treatment, and this number remained comparatively constant under ordinary conditions of growth. After heating the number of organisms per gram was reduced to as few as 60, but they increased rapidly from day to day when the soil was moistened and placed in the incubator, until in a fortnight's time they amounted to 40 millions or over per gram. The increase in fertility proceeded *pari passu* with the increased rate of production of ammonia, which in its turn depended on the increase in the number of organisms.

It was evident from the experiments that the heating had removed a factor present in ordinary soil which inhibited the development of the bacteria beyond a certain point, and it was found that the untreated soil contained a number of large organisms—protozoa, amœbæ, &c., which derive their sustenance from living bacteria. Under normal conditions an equilibrium exists between the numbers of these larger organisms and of the bacteria, and as the heating process kills off the larger organisms entirely while still leaving some of the bacteria, the latter can develop to a hitherto unprecedented extent in the absence of the factor which previously kept them in check. Exposure of the soil to the vapour of chloroform, toluene, &c., for 48 hours, followed by its complete evaporation, has the same effect in destroying the larger organisms while leaving a certain number of the bacteria or their spores ready to develop as soon as conditions favourable to growth are obtained. With these volatile antiseptics, however, destruction of the larger organisms is not so complete nor the gain of fertility so large. It has not yet been found possible to apply these processes of partial sterilisation to increasing the fertility of soils in the open, but a commercial process has been successfully worked out for greenhouse soils, which, owing to their conditions of richness in manure, high temperature and water content, afford a specially favourable medium to the development of the larger organisms.

4. *Nitrification.*—The process of nitrification and the factors by which it has been governed have long been worked out in a practical way. For example, in the *Instruction sur la fabrication du nitre: Par les régisseurs Généraux des poudres et salpetres*, 1777, the formation of nitre beds is carefully described. They were made up of earth containing a certain amount of calcareous matter, mixed with dung and other nitrogenous residues. They were protected from the weather and carefully watered from time to time with diluted urine and other materials containing nitrogen. After two or three years, the contents of the bed were lixiviated, and the solution of calcium nitrate obtained was concentrated and treated with potassium sulphate, whereupon potassium nitrate could be crystallised out of the clarified mother-liquors. It was thus recognised that soil is capable of converting organic compounds of nitrogen into nitrates in the presence of a base like calcium carbonate, and that warmth and a certain proportion of moisture are factors favourable to the process.

That the process was due to a living agency was first demonstrated by Schloesing and Müntz in 1877. These investigators showed that the action ceased if the soil was heated to the temperature of boiling water or was kept in contact with vapour of chloroform and similar antiseptics, and further that it only took place between the temperatures of 5° and 55°.

Warington, who continued the investigation, further showed that there are two stages of the oxidation process, one being the formation of nitrite followed by its oxidation to nitrate. Cultures were obtained capable of effecting one only of these changes, but owing to the difficulties of growing the organisms on the ordinary gelatin medium, it was not until Winogradsky, in 1890, devised a medium of silica jelly containing no combined nitrogen that the organisms were finally isolated in a pure state. Winogradsky obtained from soils in all parts of the world a single organism which he called *Nitrobacter*, capable of transforming nitrites into nitrates, but he obtained two organisms, *Nitrosomanas europea* in the soils of the old world, and a second *Nitrococcus javanesis* from the soils of Java, America, and Australia, which will transform ammonia into nitrites. The conditions of the activity of these organisms appear to be the absence of excess of organic matter, a neutral or faintly alkaline medium with some base in reserve to combine with the nitric acid produced, and the absence of any excess of alkaline carbonates or chlorides. It has been found possible to accustom the organism by successive cultivations to a toleration of ammoniacal and organic solutions much stronger than would normally inhibit its development. The organism derives the carbon necessary to its growth from carbonates in the culture medium or carbon dioxide in the air with which it is supplied. The nitrifying organisms are confined, as indeed are all bacteria, to the surface layers of the soil, being rarely present in subsoils at greater depth than 2 ft. They may be entirely absent from the soils of heaths of peaty bogs which are acid in their reaction, but are abundant in waters of shallow wells and rivers. Their development is promoted by warmth, by stirring the soil, and by free aeration. It was formerly considered that as the higher plants obtain their combined nitrogen almost