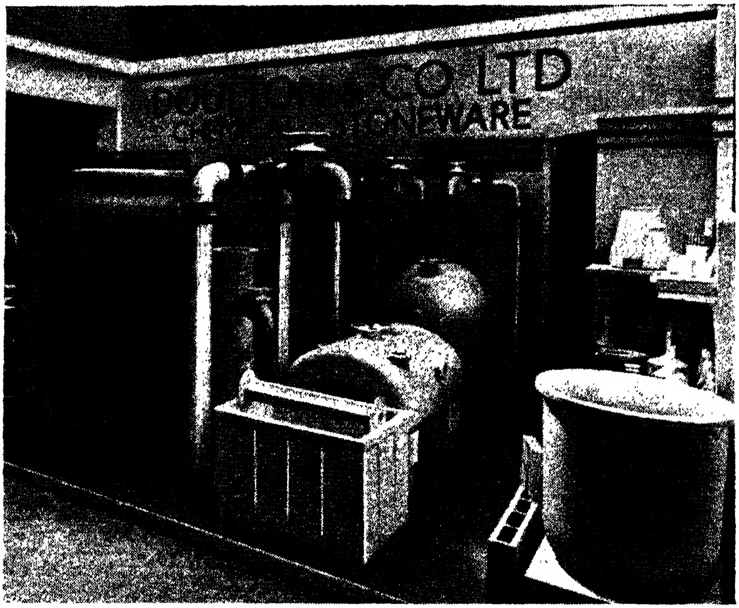
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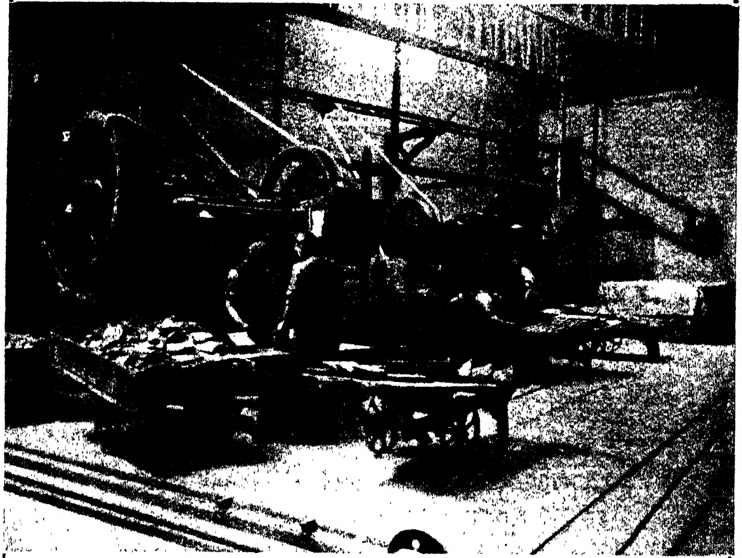

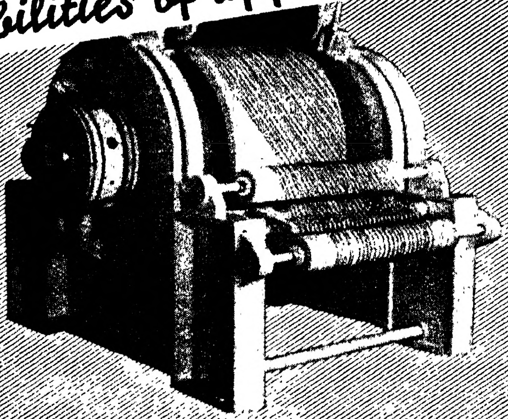

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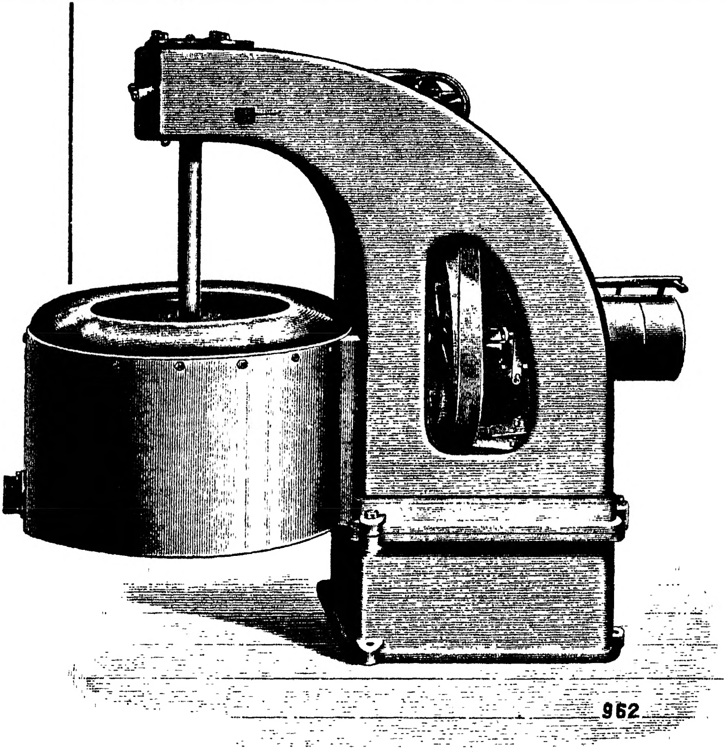
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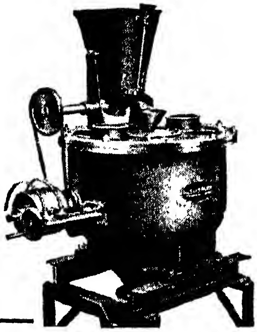

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Abbreviated Title.	Full Title.
Acta Acad. Åboensis (Math. Phys.)	Acta Academiae Åboensis (Mathematica et Physica).
Acta Brev. Néerl.	Acta Brevia Néerlandica de Physiologia, Pharmacologia, Microbiologia, etc.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Amer. Dyestuff Rep.	American Dyestuff Reporter.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Hyg.	The American Journal of Hygiene.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Trop. Med.	The American Journal of Tropical Medicine.
Amer. Min.	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Farm. Bioquím.	Anales de Farmacia y Bioquímica (Buenos Aires).
Anal. Fís. Quím.	Anales de la Sociedad Española Física y Química.
Analyst	The Analyst.
Angew. Chem.	Angewandte Chemie (formerly Zeitschrift für angewandte Chemie).
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Acad. Scient. Fennicae	Annales Academiae Scientiarum Fennicae.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. analyt.	Annales de Chimie analytique et de Chimie appliquée.
Ann. Chim. appl.	Annali di Chimica applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique (now divided see *Ann. Chim.* and *Ann. Physik.*).
Ann. Falsif.	Annales des Falsifications et des Fraudes.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Reports	Annual Reports of the Chemical Society.
Ann. Rept. Exp. Sta. Cheshunt	Cheshunt Agricultural Experiment Station Annual Reports.
Ann. Rev. Biochem.	Annual Review of Biochemistry.
Ann. Sec. Anal. Phys. Chem.	Annales du Secteur d'Analyse physicochimique, Institut de Chimie générale (U.R.S.S.).
Ann. Soc. sci. Bruxelles	Annales de la Société scientifique de Bruxelles.
Anzeiger Akad. Wiss. Wien	Anzeiger der Akademie der Wissenschaften in Wien.
Arch. Eisenhüttenw.	Archiv für das Eisenhüttenwesen.
Arch. internat. Pharm. Thérap.	Archives internationales de Pharmacodynamie et de Thérapie.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Schiff. Trop. Hyg.	Archiv für Schiffs- und Tropenhygiene, Pathologie und Therapie exotischer Krankheiten.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kemi, Min. Geol.	Arkiv für Kemi, Mineralogi och Geologi.
Astrophys. J.	The Astrophysical Journal.
Atti R. Accad. Lincei	Atti (Rendiconti) della Reale Accademia Nazionale dei Lincei. Classe di scienze fisiche, matematiche e naturali, Roma.

Abbreviated Title.	FULL TITLE.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschung in Kurashiki.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Bodenk. Pflanzenernähr.	Bodenkunde und Pflanzenernährung.
Boll. Soc. ital. Biol. sperim.	Bolletino della Società italiana di Biologia sperimentalla.
Bot. Gaz.	The Botanical Gazette.
Brennstoff-Chem.	Brennstoff-Chemie.
Brit. J. Exp. Path.	The British Journal of Experimental Pathology.
Brit. Med. J.	The British Medical Journal.
Bul. Soc. Chim. România	Buletinul Societătii de Chimie din România.
Bul. Soc. Ştiinţe Cluj	Buletinul Şocietătii de Ştiinţe din Cluj.
Bull. Acad. Méd.	Bulletin de l'Académie de Médicine.
Bull. Acad. polonaise.	Bulletin internationale de l'Académie polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique : Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Roumaine	Bulletin de la Section scientifique de l'Académie Roumaine.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Imp. Forestry Exp. Stat. Tokyo	Bulletin of the Imperial Forestry Experiment Station, Tokyo.
Bull. Inst. Phys. Chem. Res. Japan	Bulletin of the Institute of Physical and Chemical Research, Japan.
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.
Bull. Soc. Path. exot.	Bulletin de la Société de Pathologie exotique.
Canadian J. Res.	Canadian Journal of Research.
Canadian Med. Assoc. J.	The Canadian Medical Association Journal.
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Paläontologie.
Chem. and Ind.	Chemistry and Industry.
Chem. Fabr.	Die Chemische Fabrik.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. News	The Chemical News (now discontinued).
Chem. Reviews	Chemical Reviews.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Contr. Boyce Thompson Inst.	Contributions from the Boyce Thompson Institute.
Current Sci.	Current Science.
Deutsche med. Woch.	Deutsche medizinische Wochenschrift.
Edin. Med. J.	Edinburgh Medical Journal.
Gazzetta	Gazzetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.

Abbreviated Title.	FULL TITLE.
Helv. Physica Acta	Helvetica Physica Acta.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry: Analytical Edition.
Ind. Med. Gaz.	The Indian Medical Gazette.
Indian J. Med. Res.	Indian Journal of Medical Research.
Indian J. Physics	Indian Journal of Physics.
J.	Journal of the Chemical Society.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceramic Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Appl. Chem. Russia	Journal of Applied Chemistry, Russia (Zhurnal prikladnoi Chimii).
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Bact.	Journal of Bacteriology.
J. Biochem. Japan	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Educ.	Journal of Chemical Education.
J. Chem. Physics	The Journal of Chemical Physics.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Dent. Res.	The Journal of Dental Research.
J. Exper. Med.	Journal of Experimental Medicine.
J. Gen. Chem. Russia	Journal of General Chemistry (U.S.S.R.) (formerly chemical part of the Journal of the Physical and Chemical Society of Russia).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Inst. Brew.	Journal of the Institute of Brewing.
J. Nutrition	Journal of Nutrition.
J. Officiel	Journal officiel de l'Afrique occidentale.
J. Org. Chem.	The Journal of Organic Chemistry.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	The Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. N.S.W.	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Nat. Bur. Stand.	Journal of Research of the National Bureau of Standards (formerly Bureau of Standards Journal of Research).
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (now Journal of General Chemistry, Russia).
J. Sci. Hiroshima Univ.	Journal of Science of the Hiroshima University.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan.
J. Text. Inst.	Journal of the Textile Institute.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.

Abbreviated Title.	FULL TITLE.
Jahresber.	Jahresbericht über die Fortschritte der Chemie (ceased 1910).
Jernk. Ann.	Jernkontorets Annaler.
Keem. Teated	Keemia Teated.
Klin. Woch.	Klinische Wochenschrift.
Kolloid-Z.	Kolloid-Zeitschrift.
Lancet	The Lancet.
Magyar Chem. Fol.	Magyar Chemiai Folyóirat (Hungarian Chemical Journal).
Med. Parasit. and Parasit. Dis.	Medical Parasitology and Parasitic Diseases (Moscow).
Mercks Jahresber.	Mercks Jahresbericht.
Microbiol. U.S.S.R.	Microbiology (Journal of General, Agricultural and Industrial Microbiology, U.S.S.R.).
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nach. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
New England J. Med.	New England Journal of Medicine.
P.	Proceedings of the Chemical Society (discontinued 1914).
Paper Trade J.	Paper Trade Journal.
Per. Min.	Periodico di Mineralogia.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Ztg.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phot. Ind.	Photographische Industrie.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sowjetunion	Physikalische Zeitschrift der Sowjetunion.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Plant Physiol.	Plant Physiology.
Pogg. Ann.	Poggendorffs Annalen (now Annalen der Physik).
Proc. Amer. Gas Assoc.	Proceedings of the American Gas Association.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Science.
Proc. Iowa Acad. Sci.	Proceedings of the Iowa Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam (Proceedings, English version).
Proc. Leeds Phil. Soc.	Proceedings of the Leeds Philosophical and Literary Society (Scientific Section).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nat. Acad. Sci. India	Proceedings of the National Academy of Sciences, India.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.

Abbreviated Title.	Full Title.
Proc. Staff Meetings Mayo Clinic	Proceedings of the Staff Meetings of the Mayo Clinic.
Proc. Univ. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Quart. Bull. Hlth. Org. League of Nations	Quarterly Bulletin of the Health Organization of the League of Nations.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Rec. Mal. Surv. India	Records of the Malaria Survey of India.
Rec. Trav. bot. néerl.	Recueil des Travaux botaniques néerlandais.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Fac. Sci. Univ. Cagliari	Rendiconti seminario Facoltà Scienze Università di Cagliari.
Rev. Chim. pura appl.	Revista de Chimica pura e applicada (Ôrgao de Sociedade Portuguêsa de Química e Física).
Rev. Mod. Physics	Reviews of Modern Physics.
Rev. Soc. Argentin. Biol.	Revista de la Sociedad Argentina de Biologia.
Revue d'Immun.	Revue d'Immunologie.
Ric. Sci.	La Ricerca scientifica ed il Progresso tecnico nell' Economia nazionale.
Schweiz. med. Woch.	Schweizerische medizinische Wochenschrift.
Sci. J. Royal Coll. Science	The Scientific Journal of the Royal College of Science.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Nat. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Rep. Tôhoku	Scientific Reports, Tôhoku Imperial University.
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collection.
Soil Sci.	Soil Science.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tech. Phys. U.S.S.R.	Technical Physics of the U.S.S.R.
Trans. Butlerov Inst. Chem. Tech. Kazan	Transactions of the Butlerov Institute for Chemical Technology of Kazan.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Trop. Med. Hyg.	Transactions of the Royal Society of Tropical Medicine and Hygiene.
Tsch. Min. Petr. Mitt.	Tschermaks Mineralogische und Petrographische Mitteilungen (Zeitschrift für Kristallographie, Mineralogie, und Petrographie, Abteilung B).
Ukrain. Chem. J.	Ukrainian Chemical Journal (Ukrainskiĭ Khemichniĭ Zhurnal).
Verhandl. deut. physikal. Ges.	Verhandlungen der deutschen physikalischen Gesellschaft.
Vers. K. Akad. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Verslagen van de Gewone Vergadering der Afdeeling Natuurkunde.
Videnskaps.-Skrifter, Matemat.-Naturv. Klasse, Kristiania	Videnskapsselskapets-Skrifter. I, Matematisk-Naturvidenskapelig Klasse, Kristiania (now Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo).
Wien. med. Woch.	Wiener medizinische Wochenschrift.
Wisconsin Agric. Exp. Sta. Res. Bull.	Wisconsin Agricultural Experiment Station Research Bulletins.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Woch. Brau.	Wochenschrift für Brauerei.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie (now Angewandte Chemie).

Abbreviated Title.	FULL TITLE.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische Chemie).
Z. Immunität.	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. tech. Physik	Zeitschrift für technische Physik.
Z. Vitaminforschung	Zeitschrift für Vitaminforschung.
Zentr. Bakt. Par.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.

ERRATA.

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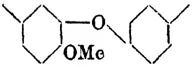
Page

353 *In formulæ* (V) *and* (VI), *for*



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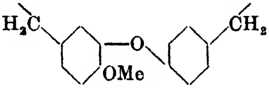

458 In ref. 62, for "*ibid.*," read "*Z. anal. Chem.*"

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

RADIOACTIVITY AND SUB-ATOMIC PHENOMENA.

DURING the year no entirely new line of nuclear research has been opened. The study of nuclear reactions has now reached the stage where it is important to collect a large quantity of precise data, and the energy changes involved have been particularly examined. The existence of a peculiar selective absorption of very slow neutrons in atomic nuclei has led to the production of new theoretical ideas about nuclear structure. Bohr has suggested that energy supplied to a nucleus may be extensively distributed over its components (see p. 30), and the theory of Breit and Wigner involves similar ideas of the energy levels of the nucleus as a whole.

A theoretical survey of a large part of nuclear physics has appeared.[1] The problems of the behaviour of the cosmic radiation, though not of its origin, are gradually assuming more definite form.

ISOTOPIC CONSTITUTION OF THE ELEMENTS.

A good deal of work has been done during the year with mass spectrographs. New instruments of this type have been described by A. J. Dempster,[2] K. T. Bainbridge and E. B. Jordan [3] and by M. B. Sampson and W. Bleakney.[4] New sources of ions are also described.[2,3,5] F. W. Aston [6] has made some improvements in his design of mass spectrograph, and has applied it mainly to the precise determination of atomic masses. These instruments have been used in the discovery of new isotopes, the determination of isotope abundance ratios, and the precise determination of nuclear masses.

An isotope ^{5}Li [7] was discovered in the emission from a platinum

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[1] H. A. Bethe and W. Bacher, *Rev. Mod. Physics*, 1936, **82**, 8.

[2] *Proc. Amer. Phil. Soc.*, 1935, **75**, 755.

[3] *Physical Rev.*, 1936, **50**, 282.

[4] *Ibid.*, p. 456.

[5] J. P. Blewett and E. J. Jones, *ibid.*, p. 464; S. L. Ch'u, *ibid.*, p. 212.

[6] *Nature*, 1936, **137**, 357.

[7] A. K. Brewer, *Physical Rev.*, 1936, **49**, 635.

filament impregnated with lithium, but this was not confirmed by other workers.[4] A special search was made for ^{8}Be,[8] since this nucleus appears as a product in the current interpretations of many nuclear reactions,[9] often recoiling intact with considerable energy. On the basis of nuclear mass considerations ^{8}Be appears to be a strongly bound element.[10] It was not found in the mass spectrograph analysis, with a detection limit of 1 part in 10^{4}. The appearance of induced radioactivity under neutron bombardment has led to a search for new isotopes of several elements, since the known isotopes were not considered sufficient to explain the different types of radioactivity observed. No third isotope was found for ^{79,81}Br,[11] which shows three decay periods when activated with slow neutrons. The limits of detection varied from $\frac{1}{400}$ for 78, 82 up to much larger values. No third isotope was found for ^{115,113}In.[12,4] In the case of ^{59}Co an isotope ^{57}Co has been found.[13] Bainbridge and Jordan have applied their mass spectrograph [3] to the problem of the existence of isobaric pairs of stable elements, differing by one unit in atomic number. According to some theories of nuclear stability, such pairs should not exist.[14] Previous mass-spectrograph work has often been complicated by the existence of hydrides, but in Bainbridge and Jordan's work hydrogen-free conditions were obtained and $^{113}_{49}$In was found isobaric with $^{113}_{48}$Cd, $^{115}_{49}$In with $^{115}_{50}$Sn, $^{123}_{52}$Te isobaric with $^{123}_{51}$Sb. The theoretical consequences of this are discussed. Other isotopes found by the mass spectrograph during the year include ^{22}Na,[15] ^{58}Fe,[16,17] ^{64}Ni,[17] ^{84}Sr,[12,4] ^{102}Mo,[18] ^{134}Ba,[4,19] ^{130,132}Ba,[18] ^{136,138}Ce.[18] A number of determinations of abundance ratios have been made with the mass spectrograph and in the case of oxygen[20] some variation has been found between various sources.

The new atomic masses observed by Aston [6] are in good accord

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[8] W. Bleakney, J. P. Blewett, R. Sherr, and R. Smoluchowski, *Physical Rev.*, 1936, **50**, 545.

[9] See this report, p. 20.

[10] M. L. Oliphant, *Nature*, 1936, **137**, 396; cf. N. K. Saha, *Proc. Indian Acad. Sci.*, 1936, **6**, 110.

[11] J. P. Blewett, *Physical Rev.*, 1936, **49**, 900.

[12] J. P. Blewett and M. B. Sampson, *ibid.*, p. 778.

[13] M. B. Sampson, L. N. Ridenour, and W. Bleakney, *ibid.*, **50**, 382.

[14] Cf. K. Sitte, *Z. Physik*, 1935, **96**, 512.

[15] A. K. Brewer, *Physical Rev.*, 1936, **49**, 856; but see ref. (4).

[16] J. de Gier and P. Zeeman, *Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 959.

[17] A. J. Dempster, *Physical Rev.*, 1936, **50**, 98.

[18] J. de Gier and P. Zeeman, *Proc. K. Akad. Wetensch. Amsterdam*, 1936, **39**, 327.

[19] A. J. Dempster, *Physical Rev.*, 1936, **49**, 947.

[20] W. Bleakney and J. A. Hipple, *ibid.*, 1935, **47**, 800.

with the values obtained from nuclear transformations.[10] It is interesting to note that mass differences of the heavy elements can now be obtained sufficiently accurately to reveal the mass equivalent of the energy emitted in their radioactive transformations.[21]

Spectroscopic Methods.—The method of hyperfine structure of spectral lines has been used to check the abundances of the lead [22] and the platinum [23] isotopes, and the cadmium isotopes have been examined in the band spectrum of CdH, CdD.[24] The elaborate corrections necessary to obtain isotopic mass ratios from band spectra have been worked out by W. W. Watson [25] and applied to the ratios ${}^2_1H/{}^1_1H$, the value obtained agreeing with that of Aston. The hyperfine structure data on nuclear spin have been used [26] to formulate a set of rules for the building up of atomic nuclei, which agree with the isotope abundance data.

NUCLEAR TRANSMUTATIONS.

The work in this field has been directed largely to the measurement of the energies involved in nuclear reactions and the excitation functions, *i.e.*, the probability of reaction considered as a function of the energy of the bombarding particle. The energies have been largely used in the determination of differences in nuclear mass, and a considerable amount of data has been acquired on the energy levels of lighter nuclei.

α-Particles.—Detailed investigations have been made of the transmutations of several nuclei under α-particle bombardment. The reactions are of the (α; p) type [27] first investigated by Rutherford, in which the product nucleus is stable.

The maximum energy of the protons may be calculated from the conservation of energy and momentum, a quantity of energy equivalent to the mass difference between initial and product nuclei appearing in the reaction. The proton may, however, carry away less than the full energy of the transformation, the product nucleus being left in an excited state, which subsequently emits a γ-ray.[28]

The investigation of the energies of the proton groups gives, therefore, mass differences between nuclei and the energies of nuclear

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[21] A. J. Dempster, *Nature*, 1936, **138**, 120, 201.

[22] J. L. Rose and R. K. Stranathan, *Physical Rev.*, 1936, **49**, 916.

[23] S. Tolansky and E. Lee, *Nature*, 1936, **137**, 908.

[24] A. Heiner and E. Hulthen, *Naturwiss.*, 1936, **24**, 377.

[25] *Physical Rev.*, 1936, **49**, 70.

[26] H. Schüler and H. Korsching, *Z. Physik*, 1936, **102**, 373.

[27] This notation is used to denote a change in which an α-particle is captured and a proton emitted. A similar notation is used for proton, deuteron, neutron reactions; cf. *Ann. Reports*, 1935.

[28] H. J. von Baeyer, *Z. Physik*, 1935, **95**, 417.

excited states. O. Haxel[29] found that the reactions Mg (α; p) Al, Si (α; p) P, S (α; p) Cl gave very similar proton spectra consisting in each case of three groups. The excited states are given in Table I. A. N. May and R. Vaidyanathan[30] find that the reactions F (α; p) Ne, Na (α; p) Mg, P (α; p) S each give four proton groups corresponding with three excited levels differing by about 1 M.E.V. C. J. Brasefield and E. Pollard[31] find for S (α; p) Cl three groups generally similar to those of Haxel, while for K (α; p) Ca, Cl (α; p) A, P (α; p) S they find excited levels differing by about 1·5 M.E.V. From the full energy proton group of S (α; p) Cl they calculated the mass of ^{32}S from Bainbridge's ^{35}Cl value. The evidence, then, points to the existence of homologous series of nuclei differing by four units in mass and two in atomic number. These may be correlated with the existence of α-particles as such in the nuclei (Haxel) or with the formation of successive shells of neutrons and protons. The homologous series ^{27}Al, ^{31}P, ^{35}Cl does not appear to extend to ^{11}B and ^{15}N, which have different level systems.[32]

TABLE I.

Energy of α-particle reactions : excitation levels of nuclei from transitions. A (α; p) $\longrightarrow$ B (+ Q).

	Reaction.	Energy change, Q (M.E.V.).		Product nucleus.	Energy of excited levels (M.E.V.).
33	^{14}N (α; p) ^{17}O	− 1·4		^{17}O	1·4
29	^{24}Mg (α; p) ^{27}Al	—	$A = 4n + 3$	^{27}Al	0·8, 1·7
29	^{28}Si (α; p) ^{31}P	—		^{31}P	0·8, 1·6
29	^{32}S (α; p) ^{35}Cl	− 2·25		^{35}Cl	0·65, 1·6
31	,,	− 2·4		,,	0·5, 1·25
30	^{19}F (α; p) ^{22}Ne	+ 1·4	$A = 4n + 2$	^{22}Ne	1·5, 3·5, 4·6
30	^{23}Na (α; p) ^{26}Mg	+ 1·9		^{26}Mg	2·3, 4·0, 5·0
34	^{27}Al (α; p) ^{30}Si	+ 2·1		^{30}Si	2·3, 3·6, 5·9
30	^{31}P (α; p) ^{34}S	—			
31	,,	+ 0·0		^{34}S	1·2, 2·6, 4·6
31	^{35}Cl (α; p) ^{38}A	+ 0·1		^{39}A	—, 2·6, 4·3
31	^{39}K (α; p) ^{43}Ca	− 1·0		^{42}Ca	—, 1·3, 2·6

The transmutation function in the case of S (α; p) Cl appears to consist of an increase of transmutation probability with α-particle energy corresponding to the Gamow theory for penetration of a potential barrier. May and Vaidyanathan point out that the existence of preferred velocities for α-particle entry to the nucleus

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[29] *Physikal. Z.*, 1935, **36**, 804.

[30] *Proc. Roy. Soc.*, 1936, *A*, **155**, 519; cf. R. F. Paton, *Z. Physik*, 1934, **90**, 586.

[31] *Physical Rev.*, 1936, **50**, 296, 890.

[32] J. D. Cockroft and W. B. Lewis, *Proc. Roy. Soc.*, 1936, *A*, **154**, 246, 261.

[33] G. Stetter, *Z. Physik*, 1936, **100**, 652.

[34] W. E. Duncanson and H. Miller, *Proc. Roy. Soc.*, 1934, **146**, 396.

(resonance penetration) may give rise to groups in the proton spectrum when an inhomogeneous source of α-particles or a thick target is used. An extra group in the reaction P (α ; *p*) S is probably accounted for in this way.

Protons.—The transmutation of some of the light elements by proton bombardment has been studied in detail. The excitation function for the reaction

$$^7\text{Li} + {}^1_1\text{H} \longrightarrow 2^4\text{He}$$

has been determined from 23 kv.,[35] 40—225 kv.,[36] and up to 1100 kv.[37, 38] The curve rose monotonically with energy; no specially preferred energy values (resonance) were detected. A new wave-mechanical treatment of the problem of a nucleus with a potential well under proton bombardment[39] has been given. The simpler treatment of the problem as penetration through a potential barrier is not adequate; the depth and width of the well have a marked effect on the efficiency curve. The calculation gives the position of the stationary proton levels and the mass of the ^{8}Be nucleus, and the potential well has to be adjusted to give consistent values for these data as well as fitting the excitation curve. A further calculation using "exchange forces" which vary with the velocity of the proton gives better results.[40]

The angular distribution of the α-particles produced in this reaction has been shown to be random,[41] and the variation of range with angle is in agreement with the conservation of energy and momentum.[42] If ^{8}Be is formed as an intermediate step, the fact that it does not lose energy by collision shows that its life is less than 3×10^{-14} sec.

The γ-ray emission from lithium, showing resonance at about 450 kv. and a rise at higher voltages,[37] has been confirmed and shown to arise from ^{7}Li.[43] The γ-ray emission process is independent of that which produces the α-rays; it may consist of the excitation of ^{8}Be to a state which is debarred from disintegration by a selection rule, or to the production of an excited and a normal α-particle.

A γ-ray emission from fluorine bombarded with protons[37] shows

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[35] H. D. Doolittle, *Physical Rev.*, 1936, **49**, 779.

[36] N. P. Heydenburg, C. T. Zahn, and L. D. P. King, *ibid.*, p. 100.

[37] L. R. Hafstad, N. P. Heydenburg, and M. A. Tuve, *ibid.*, **50**, 504; R. G. Herb, D. B. Parkinson, and D. W. Kent, *ibid.*, 1935, **48**, 118.

[38] L. R. Hafstad and M. A. Tuve, *ibid.*, p. 306.

[39] M. Ostrofsky, G. Breit, and D. P. Johnson, *ibid.*, 1936, **49**, 22.

[40] M. Ostrofsky, W. E. Bleick, and G. Breit, *ibid.*, p. 352.

[41] J. Giarratana and C. G. Brennecke, *ibid.*, p. 35.

[42] A. Roberts, T. Zandstra, R. Cortell, and F. E. Myers, *ibid.*, p. 783.

[43] L. H. Rumbaugh and L. R. Hafstad, *ibid.*, **50**, 681.

resonances at 328, 892, and 942 kv. and probably some weak multiple structure between 500 and 700 kv., but the reaction involved is uncertain.

The reaction

$$^{11}_{5}B + ^{1}_{1}H \longrightarrow 3^{4}_{2}He$$

has been confirmed and examined.[44] The products of disintegration have been studied by the Wilson chamber.[45] The distribution of energy among the α-particles is continuous, with a small homogeneous group superposed. The symmetrical emission of three α-particles, formerly regarded as a preferred process, is now shown to be rare, and the mechanism suggested is the formation of an excited ^{8}Be nucleus (p ; α change) and its subsequent splitting into two α-particles. The life of the excited ^{8}Be lies between 10^{-17} and 10^{-22} sec., and it is suggested that according to the uncertainty principle the excitation energy is rather indefinite and the particles emitted in the (p ; α) reaction have a velocity spread. On these assumptions the continuous distribution may be explained, the total energy released in the transmutation being 8·7 M.E.V. in accordance with the revised nuclear masses.[10] The small homogeneous group may then correspond to the reaction

$$^{11}_{5}B + ^{1}_{1}H \longrightarrow ^{8}_{4}Be + ^{4}_{2}He \ (Q = + 8{\cdot}7 \text{ M.E.V.})$$

with the mass of ^{8}Be very nearly equal to that of two α-particles. A similar argument to that above may be used to explain the deuteron reaction[46]

$$^{10}_{5}B + ^{2}_{1}H \longrightarrow 3^{4}_{2}He$$

The excitation function for the two proton–boron processes shows a marked difference,[47] the continuous distribution rising steadily with increase of bombarding voltage while the longer range group shows evidence of resonance.

W. H. Wells and E. L. Hill [48] have attempted to avoid the necessity for the nucleus $^{8}_{4}Be$ in this and similar reactions by postulating that some of the nuclear particles are coupled in sub-groups.

Deuterons.—Several new nuclear transmutations have been obtained by deuteron bombardment, and some of the formerly-known reactions have been studied in more detail. A number of excitation functions have been determined, and the energy of the product particles has been the subject of special attention. By intercompari-

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[44] J. D. Cockroft and W. B. Lewis, *Proc. Roy. Soc.*, 1936, *A*, **154**, 246.

[45] P. I. Dee and C. W. Gilbert, *ibid.*, p. 279.

[46] Cf. M. L. E. Oliphant, A. E. Kempton, and (Lord) Rutherford, *ibid.*, 1935, *A*, **150**, 241.

[47] J. H. Williams and W. H. Wells, *Physical Rev.*, 1936, **50**, 186.

[48] *Ibid.*, **49**, 858.

son of the energy liberated in the reactions with the atomic mass scale, the latter has been corrected and further various proposed nuclear reactions have been checked. This check is important, since the reactions produced by deuteron bombardment of the lighter nuclei are in general complicated.

The excitation function for the reaction

$$ {}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}n $$

has been investigated by T. W. Bonner and W. M. Brubaker.[49] The probability of transmutation rises rather slowly with the energy of the deuterons, while the yield of neutrons from the reaction

$$ {}^{9}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{10}_{5}\mathrm{B} + {}^{1}_{0}n $$

which was also studied, rises much more steeply. The neutrons produced are nearly homogeneous in energy,[50] 2·55 M.E.V., and the energy released in the reaction is 3·2 M.E.V. No γ-radiation could be detected.[51]

The reaction

$$ {}^{11}_{5}\mathrm{B} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}n $$

gives two groups of neutrons, the lower one corresponding with the production of an excited ^{12}C nucleus. The excited level of ^{12}C at about 4 M.E.V. has also been detected by J. D. Cockroft and W. B. Lewis[52] in the reaction

$$ {}^{14}_{7}\mathrm{N} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He} $$

and by Chadwick, Bothe, and others in the reaction

$$ {}^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}n $$

An investigation[53] of the neutrons from the bombardment of beryllium, boron, and carbon, which are believed to be produced by the reactions

$$ \begin{aligned} {}^{9}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{10}_{5}\mathrm{B} + {}^{1}_{0}n \\ {}^{11}_{5}\mathrm{B} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}n \\ {}^{11}_{5}\mathrm{B} + {}^{2}_{1}\mathrm{H} &\longrightarrow 3\,{}^{4}_{2}\mathrm{He} + {}^{1}_{0}n \\ {}^{10}_{5}\mathrm{B} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{11}_{6}\mathrm{C} + {}^{1}_{0}n \\ {}^{12}_{6}\mathrm{C} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{13}_{7}\mathrm{N} + {}^{1}_{0}n \\ {}^{13}_{6}\mathrm{C} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{14}_{7}\mathrm{N} + {}^{1}_{0}n \end{aligned} $$

has led to energy values for these reactions and to a revised atomic-mass scale. In addition to the neutrons of maximum energy, neutron groups of lower energy were emitted, the nuclei being left in an excited state. No satisfactory correlation has been made with the

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[49] *Physical Rev.*, 1936, **49**, 19.

[50] Cf. P. I. Dee and C. W. Gilbert, *Proc. Roy. Soc.*, 1935, *A*, **149**, 200.

[51] K. D. Alexopoulous, *Naturwiss.*, 1935, **23**, 817.

[52] *Proc. Roy. Soc.*, 1936, *A*, **154**, 246, 261.

[53] T. W. Bonner and W. M. Brubaker, *Physical Rev.*, 1936, **50**, 308.

γ-rays which accompany the bombardment.[54] The transmutation of boron, carbon, nitrogen, and oxygen by deuterons has also been studied by J. D. Cockroft and W. B. Lewis.[52] In this work the ranges of the α- and H-particles were measured. With boron, homogeneous groups of α-particles were attributed to

$$^{11}_{5}\mathrm{B} + ^{2}_{1}\mathrm{H} \longrightarrow ^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He}$$
$$^{10}_{5}\mathrm{B} + ^{2}_{1}\mathrm{H} \longrightarrow ^{8}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He}$$

while proton groups were attributed to

$$^{10}_{5}\mathrm{B} + ^{2}_{1}\mathrm{H} \longrightarrow ^{11}_{5}\mathrm{B} + ^{1}_{1}\mathrm{H}$$

and a continuous distribution of α-particles to

$$^{10}\mathrm{B} + ^{2}\mathrm{H} \longrightarrow 3^{4}\mathrm{He}$$

and with less certainty to

$$^{11}\mathrm{B} + ^{2}\mathrm{H} \longrightarrow 3^{4}\mathrm{He} + ^{1}_{0}n$$

The energy values of several reactions with carbon, nitrogen, and oxygen were determined and used to amend the mass scale.

A new group of α-particles from carbon probably arises from $^{13}\mathrm{C} + ^{2}\mathrm{H} \longrightarrow ^{11}\mathrm{B} + ^{4}\mathrm{He}$, though the energy balance with other reactions is not satisfactory.

During the experiments on boron, an attempt was made to detect the recoil of $^{8}\mathrm{Be}$, a nucleus which rather frequently appears in proposed transmutation reactions. The energy data lead to the conclusion that the mass of $^{8}\mathrm{Be}$ should be slightly greater than that of two α-particles :

$$^{8}\mathrm{Be} \longrightarrow 2^{4}\mathrm{He} + 0{\cdot}3\ \mathrm{M.E.V.}\ (\text{cf. p. } 20)$$

The production of β-radioactive elements of short life from lithium, boron, and fluorine [55] has been further investigated.[56] The radio-elements are now believed to be $^{8}\mathrm{Li}$, $^{12}\mathrm{B}$, and $^{20}\mathrm{F}$, formed by $(d;\,p)$ processes. The corresponding proton emission has been found for lithium and fluorine and the energy balances calculated. The protons from boron have not been definitely identified, but their energy is $< 2{\cdot}5$ M.E.V. These radioactive elements are all believed to have atomic weights given by $2Z + 2$, containing two more neutrons than protons. The positron-emitting elements $^{13}\mathrm{N}$ [$^{12}\mathrm{C}\ (d;\,n)^{13}\mathrm{N}$], $^{15}\mathrm{O}$ [$^{14}\mathrm{N}\ (d;\,n)\ ^{15}\mathrm{O}$], $^{16}\mathrm{N}$ [$^{15}\mathrm{N}\ (d;\,p)\ ^{16}\mathrm{N}$], $^{11}\mathrm{C}$ [$^{10}\mathrm{B}\ (d;\,n)\ ^{11}\mathrm{C}$] were also examined. No evidence was obtained for positron emission from $^{10}\mathrm{Be}$ or $^{14}\mathrm{C}$—these nuclei are either stable or are not formed by $^{9}\mathrm{Be}\ (d;\,p)$ and $^{13}\mathrm{C}\ (d;\,p)$. For all these radio-

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[54] H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen, *Physical Rev.*, 1935, **47**, 782.

[55] Crane, Delsasso, Fowler, and Lauritsen, *ibid.*, pp. 971, 887; **48**, 848.

[56] *Idem*, *ibid.*, 1936, **49**, 561.

elements the positron or electron spectra were determined. There is some evidence[57] for a radioactive substance ^{10}Be with a very long life (> 10 years) and a ^{14}C with a half-life of about 3 months.

The deuteron bombardment of heavier elements has led to several interesting transmutations. Magnesium gives a composite β-radioactivity attributed to the processes[58]

$$^{26}_{12}\text{Mg} + {}^{2}_{1}\text{H} \longrightarrow {}^{27}_{12}\text{Mg} + {}^{1}_{1}\text{H} \qquad {}^{27}_{12}\text{Mg} \xrightarrow[10\text{ mins.}]{\beta} {}^{27}_{13}\text{Al}$$

$$^{26}_{12}\text{Mg} + {}^{2}_{1}\text{H} \longrightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He} \qquad {}^{24}_{11}\text{Na} \xrightarrow[15\cdot 8\text{ hrs.}]{\beta} {}^{24}_{12}\text{Mg}$$

The transmutation function for the latter process follows a Gamow relation; that for the former reaction agrees with the theory of J. R. Oppenheimer and M. Phillips[59] based on the idea that the deuteron splits into a proton and a neutron, only the neutron penetrating the nuclear potential barrier. S. N. Van Voorhis[60] finds two radioactive substances from copper, which he ascribes to (*d*; *p*) reactions with the two stable isotopes. He considers that ^{64}Cu may decay *either* to ^{64}Zn with emission of an electron or to ^{64}Ni with emission of a positron, since the half-life of positron and electron activities was the same (12·8 hrs.).

Argon[61] gives an electron-emitting radioactive substance of half-life 110 minutes. This is almost certainly ^{41}A formed by a (*d*; *p*) reaction. It behaves chemically like argon. The excitation function agrees with the theory of Oppenheimer and Phillips. A weak activity of the same type was excited in argon by intense neutron bombardment. The β[62]- and γ[63]-emission from ^{41}A has been investigated. The former seems to consist of two groups with upper energy limits at about 1·5 M.E.V. and 5 M.E.V., and the latter consists of a single line with energy 1·4 M.E.V. Copper, zinc, antimony, ruthenium, bismuth, and tin give radioactive products when bombarded with deuterons of 5 M.E.V.[64] Copper gives ^{64}Cu, as observed by E. Fermi by neutron bombardment,[65] and some other activities of obscure origin. Zinc, antimony, and ruthenium give complex activities which cannot yet be assigned with certainty to particular nuclei. Bismuth gives radium-*E* (^{210}Bi) by a (*d*; *p*) (Oppenheimer–Phillips)

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[57] E. McMillan, *Physical Rev.*, 1936, **49**, 876.

[58] M. C. Henderson, *ibid.*, 1935, **48**, 855.

[59] *Ibid.*, p. 500; see *Ann. Reports*, 1935, **32**, 23.

[60] *Physical Rev.*, 1936, **49**, 876; **50**, 895; cf. E. O. Lawrence, E. McMillan, and R. L. Thornton, *ibid.*, 1935, **48**, 493.

[61] A. H. Snell, *ibid.*, 1936, **49**, 555.

[62] F. N. D. Kurie, J. R. Richardson, and H. C. Paxton, *ibid.*, p. 368.

[63] J. R. Richardson, *ibid.*, p. 203.

[64] J. J. Livingood, *ibid.*, **50**, 425; J. J. Livingood and G. Seaborg, *ibid.*, p. 435.

[65] *Ann. Reports*, 1935.

reaction. This represents the first artificial production of a naturally occurring radio-element. Radium-*E* decays to the α-emitter Ra-*F* (polonium) with a half-life of 5 days. The α-particle emission from this substance was detected, and the identity of the range of the particles with polonium α-particles was verified. The complex activities observed from zinc, antimony, and ruthenium indicate that the Oppenheimer–Phillips process is not the only method of attack of deuterons on the heavy nucleus. The alternative is presumably a resonance process, but excitation functions have not yet been determined. Tin also shows a complex activity, and a chemical separation showed the presence of active isotopes of indium, tin, and antimony. The antimony fraction emits both positrons and electrons, and there is some evidence that this is a branched transformation and not due merely to the presence of two different radio-elements. Platinum [66] bombarded with 5 M.E.V. deuterons gives a composite activity with emission of both positrons and electrons. A chemical separation reveals isotopes of platinum and iridium. The reactions involved possibly include

$$ {}^{192}_{78}\mathrm{Pt} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{193}_{78}\mathrm{Pt} + {}^{1}_{1}\mathrm{H} \qquad {}^{193}\mathrm{Pt} \longrightarrow {}^{193}\mathrm{Ir} + e^{+} \text{ (49 mins.)} $$
$$ {}^{196}_{78}\mathrm{Pt} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{197}_{78}\mathrm{Pt} + {}^{1}_{1}\mathrm{H} \qquad {}^{197}\mathrm{Pt} \longrightarrow {}^{197}\mathrm{Au} + e^{-} \text{ (14·5 hrs.)} $$
$$ {}^{196}_{78}\mathrm{Pt} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{194}_{77}\mathrm{Ir} + {}^{4}_{2}\mathrm{He} \qquad {}^{194}\mathrm{Ir} \longrightarrow {}^{194}\mathrm{Pt} + e^{-} $$

The transmutation functions in this case definitely show the maxima expected for a resonance process, and there is evidence that the resonance is involved in the production of iridium isotopes, the platinum isotopes being formed by an Oppenheimer–Phillips process rising monotonically with the energy of bombardment.

Neutrons.—The reaction of slow neutrons with boron

$$ {}^{10}_{5}\mathrm{B} + {}^{1}_{0}n \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} $$

has been investigated by D. Roaf,[67] using boron trifluoride in an expansion chamber, and the energy released in the reaction is found to be 0·61 M.E.V. A new value for the mass of ^{10}B was obtained. The helium obtained by bombarding boron (methyl borate) with slow neutrons has been separated and observed spectroscopically. This is the first time a product of artificial transmutation has been observed by such methods.[68]

The disintegration of nitrogen by neutrons has again been investigated in the expansion chamber.[69] The reactions observed were supposed to be

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[66] J. M. Cork and E. O. Lawrence, *Physical Rev.*, 1936, **49**, 788.

[67] *Proc. Roy. Soc.*, 1936, *A*, **153**, 568.

[68] F. A. Paneth and H. Loleit, *Nature*, 1935, **136**, 950.

[69] T. W. Bonner and W. M. Brubaker, *Physical Rev.*, 1936, **49**, 223, 778; **50**, 781.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{11}_{5}B + ^{4}_{2}He$$
$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$
$$^{14}_{7}N + ^{1}_{0}n \longrightarrow 2^{4}_{2}He + ^{7}_{3}Li$$

and the first of these reactions was supposed to be exothermic and to take place with slow neutrons. A closer consideration of the energy balance as compared with other known reactions of the nuclei involved showed that this conclusion was wrong, the reaction being endothermic ($Q = -0{\cdot}3$ M.E.V.). The reaction which does occur with slow neutrons is the (n; p) change leading to ^{14}C. The radiation of energy during the capture of fast neutrons [70] by nitrogen is not supported by these experiments.

Some additions have been made to the results on the production of radioactive nuclei by neutron bombardment; these are given in Table III.

Beryllium bombarded with neutrons and examined after a very short interval showed a strong activity of period 0·9 sec.[71] The radioactive substance was identified as a helium isotope, probably [72] ^{6}He formed by a (n : α) process. It is not produced by very slow neutrons, but is formed by neutrons of 1·5 M.E.V.[73] It emits β-rays with maximum energy about 3·7 M.E.V.

Lithium [74] bombarded with slow neutrons gives a β-emitting substance, probably ^{8}Li, with half-period 0·7 sec., and identical with the substance produced from lithium by a (d; p) reaction.[75] The discrepancies in the results obtained on the rare earths, due to the difficulties of separation, have led to a re-examination of these elements by G. Hevesy and H. Levi.[76] Their results will be found in Table III. They investigated in addition the absorption of slow neutrons by the rare-earth elements and found very large absorption cross-sections for europium, dysprosium, gadolinium, and samarium. In the cases of the last two and possibly some other elements, the induced radioactivity is very small compared with the absorption cross-section, and the product nucleus is presumably stable. The complicated system of reactions observed when uranium is bombarded with neutrons has been further investigated.[77] In addition to previously-known activities with half-lives 10 secs., 40 secs., 13 mins., 100 mins., and 3 days, an activity of 12 hours' half-life has

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[70] F. N. D. Kurie, *Physical Rev.*, 1935, **47**, 97; *Ann. Reports*, 1935, **32**, 24.

[71] T. Bjerge, *Nature*, 1936, **137**, 865.

[72] *Idem*, *ibid.*, p. 400.

[73] M. L. Oliphant, quoted in ref. 72.

[74] K. S. Knol and J. Veldkamp, *Physica*, 1936, **3**, 145.

[75] Crane, Delsasso, Fowler, and Lauritsen, *Physical Rev.*, 1935, **47**, 971; see, however, ref. 56.

[76] *Nature*, 1936, **137**, 185.

[77] (Frl.) L. Meitner and O. Hahn, *Naturwiss.*, 1936, **24**, 158.

been assigned to eka-osmium(^{237}eka-Os). Evidence is obtained for the following reactions :

$$(1)\quad {}^{238}_{92}\mathrm{U} + n \longrightarrow {}^{235}_{90}\mathrm{Th} + \alpha \xrightarrow{\beta} {}^{235}\mathrm{Pa} \xrightarrow{\beta} {}^{235}\mathrm{U} \xrightarrow{\beta} {}^{235}\text{eka-Re} \longrightarrow$$

The reaction goes with slow neutrons and ^{239}U may be formed by a (n; —) reaction and behave as an α-emitter of very short life.

$$(2)\quad {}^{238}_{92}\mathrm{U} + n \longrightarrow {}^{237}_{92}\mathrm{U} + 2n \xrightarrow[\text{40 secs.}]{\beta} {}^{237}_{93}\text{eka-Re} \xrightarrow[\text{16 mins.}]{\beta}$$
$${}^{237}_{94}\text{eka-Os} \xrightarrow[\text{12 hrs.}]{\beta} {}^{237}_{95}\text{eka-Ir}$$

The reaction requires fast neutrons, and may be of a new type in which a neutron is absorbed and two neutrons are emitted :

$${}^{238}_{92}\mathrm{U} + n \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta} {}^{239}_{93}\text{eka-Re} \xrightarrow[\text{2·2 mins.}]{\beta} {}^{239}_{94}\text{eka-Os} \xrightarrow[\text{59 mins.}]{\beta}$$
$${}^{239}_{95}\text{eka-Ir} \xrightarrow[\text{3 days}]{}$$

The reaction of neutrons with thorium has been investigated;[78] the thorium salt used had been chemically kept free from its isotopic radioactive products of moderate life. The processes suggested are

$${}^{232}_{90}\mathrm{Th} + n \longrightarrow {}^{229}_{88}\mathrm{Ra} + \alpha;\ {}^{229}_{88}\mathrm{Ra} \xrightarrow{\beta} {}^{229}_{89}\mathrm{Ac} \xrightarrow{\beta} {}^{229}_{90}\mathrm{Th} \xrightarrow{\beta}$$
$${}^{229}_{91}\mathrm{Pa} \xrightarrow{\alpha} {}^{225}_{88}\mathrm{Ac} \xrightarrow{\beta} {}^{225}_{90}\mathrm{Th}$$

The two isotopes of actinium have half-lives of 3·5 and 42 hours, and an isotope of thorium a half-life of 25 mins.

γ-Rays.—The disintegration of nuclei by γ-rays (nuclearphilic effect [79]) has been further investigated in beryllium and deuterium.[80] No other reactions of this type have been discovered, and from the present nuclear masses it appears that no other reactions among the light elements are energetically possible using 2—3 M.E.V. γ-rays.[81] In the case of ^{2}H the threshold value for the reaction

$${}^{2}\mathrm{H} + h\nu \longrightarrow {}^{1}\mathrm{H} + n$$

is found to be 2·26 M.E.V.[82] The mass of the neutron may be calculated from this result to be 1·009.

The threshold for $^{9}\mathrm{Be} + h\nu \longrightarrow {}^{8}\mathrm{Be} + n$ is found to be 1·6 M.E.V.[83] The efficiency of the process (yield per quantum) falls

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[78] E. Rona and E. Neuninger, *Naturwiss.*, 1936, **24,** 491.

[79] Nuclear photo-effect.

[80] D. P. Mitchell, F. Rasetti, G. A. Fink, and G. B. Pegram, *Physical Rev.*, 1936, **50,** 189; S. Nishida, *Japan. J. Physics*, 1936, **11,** 9.

[81] N. Feather, " Nuclear Physics," Cambridge, 1936.

[82] J. Chadwick, N. Feather, and Bretscher, quoted in ref. 81.

[83] J. Chadwick and M. Goldhaber, *Proc. Roy. Soc.*, 1935, *A*, **151,** 479; cf. G. Ising and M. Helde, *Nature*, 1936, **137,** 273.

TABLE II.

Energies of some nuclear reactions (in 10^6 electron-volts).

(Note : 1 M.E.V. corresponds with 0·00106 unit of atomic mass.)

	Q.	
${}_{1}^{2}\mathrm{H} + \gamma \longrightarrow {}_{1}^{1}\mathrm{H} + {}_{0}^{1}n$	2·26	82
${}_{1}^{2}\mathrm{H} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{2}^{3}\mathrm{He} + {}_{0}^{1}n\ (+Q)$	3·2	49
${}_{1}^{2}\mathrm{H} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{2}^{3}\mathrm{He} + {}_{1}^{1}\mathrm{H}\ (+Q)$	4·0	85
${}_{3}^{6}\mathrm{Li} + {}_{0}^{1}n \longrightarrow {}_{1}^{3}\mathrm{H} + {}_{2}^{4}\mathrm{He}$	4·3	86
${}_{3}^{6}\mathrm{Li} + {}_{1}^{1}\mathrm{H} \longrightarrow {}_{2}^{3}\mathrm{He} + {}_{2}^{4}\mathrm{He}$	3·5	87
${}_{3}^{6}\mathrm{Li} + {}_{1}^{2}\mathrm{H} \longrightarrow 2\,{}_{2}^{4}\mathrm{He}$	22·1	88
${}_{3}^{6}\mathrm{Li} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{3}^{7}\mathrm{Li} + {}_{1}^{1}\mathrm{H}$	5·0	89
${}_{3}^{7}\mathrm{Li} + {}_{1}^{1}\mathrm{H} \longrightarrow 2\,{}_{2}^{4}\mathrm{He}$	17·1	88
${}_{3}^{7}\mathrm{Li} + {}_{1}^{2}\mathrm{H} \longrightarrow 2\,{}_{2}^{4}\mathrm{He} + {}_{0}^{1}n$	14·3	90, 91
${}_{3}^{7}\mathrm{Li} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{4}^{8}\mathrm{Be} + {}_{0}^{1}n$	14·3	91
${}_{4}^{9}\mathrm{Be} + \gamma \longrightarrow {}_{4}^{8}\mathrm{Be} + {}_{0}^{1}n$	1·6	83
${}_{4}^{9}\mathrm{Be} + {}_{1}^{1}\mathrm{H} \longrightarrow {}^{8}\mathrm{Be} + \mathrm{D}$	0·5	92
${}_{4}^{9}\mathrm{Be} + {}_{1}^{1}\mathrm{H} \longrightarrow {}_{3}^{6}\mathrm{Li} + {}_{2}^{4}\mathrm{He}$	3·6	92
${}_{4}^{9}\mathrm{Be} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{3}^{7}\mathrm{Li} + {}_{2}^{4}\mathrm{He}$	7·2	92
${}_{4}^{9}\mathrm{Be} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{4}^{10}\mathrm{Be} + {}_{1}^{1}\mathrm{H}$	4·7	92
${}_{4}^{9}\mathrm{Be} + {}_{1}^{2}\mathrm{He} \longrightarrow {}_{5}^{10}\mathrm{B} + {}_{0}^{1}n$	4·25	53
${}_{4}^{9}\mathrm{Be} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{4}^{8}\mathrm{Be} + {}_{1}^{3}\mathrm{H}$	4·5	92
${}_{5}^{10}\mathrm{B} + {}_{0}^{1}n \longrightarrow {}_{3}^{7}\mathrm{Li} + {}_{2}^{4}\mathrm{He}$	0·61	67
${}_{5}^{10}\mathrm{B} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{5}^{11}\mathrm{B} + {}_{1}^{1}\mathrm{H}$	9·1, 7·0, 4·6	51
${}_{5}^{10}\mathrm{B} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{4}^{8}\mathrm{Be} + {}_{2}^{4}\mathrm{He}$	17·5	51
${}_{5}^{10}\mathrm{B} + {}_{1}^{2}\mathrm{H} \longrightarrow 3\,{}_{2}^{4}\mathrm{He}$	17·5	51
${}_{5}^{10}\mathrm{B} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{6}^{11}\mathrm{C} + {}_{0}^{1}n$	6·2, 4·0	53
${}_{5}^{10}\mathrm{B} + {}_{2}^{4}\mathrm{He} \longrightarrow {}_{6}^{13}\mathrm{C} + {}_{1}^{1}\mathrm{H}$	3·1	93
${}_{5}^{11}\mathrm{B} + {}_{1}^{1}\mathrm{H} \longrightarrow 3\,{}_{2}^{4}\mathrm{He}$	8·7	45
${}_{5}^{11}\mathrm{B} + {}_{1}^{1}\mathrm{H} \longrightarrow {}_{4}^{8}\mathrm{Be} + {}_{2}^{4}\mathrm{He}$	8·7	45
${}_{5}^{11}\mathrm{B} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{4}^{9}\mathrm{Be} + {}_{2}^{4}\mathrm{He}$	8·1	51
${}_{5}^{11}\mathrm{B} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{6}^{12}\mathrm{C} + {}_{0}^{1}n$	13·5, 9·1	53
${}_{6}^{12}\mathrm{C} + {}_{0}^{1}n \longrightarrow {}_{4}^{9}\mathrm{Be} + {}_{2}^{4}\mathrm{He}$	− 7	94
${}_{6}^{12}\mathrm{C} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{6}^{13}\mathrm{C} + {}_{1}^{1}\mathrm{H}$	2·7	51
${}_{7}^{14}\mathrm{N} + {}_{0}^{1}n \longrightarrow {}_{5}^{11}\mathrm{B} + {}_{2}^{4}\mathrm{He}$	− 0·3	69
${}_{7}^{14}\mathrm{N} + {}^{1}n \longrightarrow {}_{6}^{14}\mathrm{C} + {}_{1}^{1}\mathrm{H}$	0·6	69
${}_{7}^{14}\mathrm{N} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{7}^{15}\mathrm{N} + {}_{1}^{1}\mathrm{H}$	8·5, 3·3	51
${}_{7}^{14}\mathrm{N} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{6}^{12}\mathrm{C} + {}_{2}^{4}\mathrm{He}$	13·2, 8·9	51
${}_{8}^{16}\mathrm{N} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{8}^{17}\mathrm{O} + {}^{1}\mathrm{H}$	1·9	51
${}_{8}^{16}\mathrm{O} + {}_{1}^{2}\mathrm{H} \longrightarrow {}_{7}^{14}\mathrm{N} + {}_{2}^{4}\mathrm{He}$	2·95	51

For the calculation of masses from data of this type, see, *e.g.*, refs. 51, 53.

with increasing γ-ray energy rather like that of the photoelectric effect in the extra-nuclear atom.[84]

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[84] R. Fleischmann and W. Gentner, *Z. Physik*, 1936, **100**, 440.

[85] P. I. Dee and C. W. Gilbert, *Proc. Roy. Soc.*, 1935, *A*, **149**, 200.

[86] J. Chadwick and M. Goldhaber, *Proc. Camb. Phil. Soc.*, 1935, **31**, 612; see also ref. 81.

[87] P. I. Dee, *Proc. Roy. Soc.*, 1935, *A*, **148**, 623.

[88] M. L. Oliphant, B. B. Kinsey, and (Lord) Rutherford, *ibid.*, 1935, *A*, **149**, 406.

Slow Neutrons.—A great deal of work has been done on the mechanism by which neutrons are slowed down by passage through matter and on the capture of slow neutrons by nuclei. Experiments show that the efficiency of neutrons in causing transmutation and the cross-section for absorption of slow neutrons were in some cases increased by cooling the paraffin or other hydrogen-rich material in which the neutrons were slowed down.[5] The interpretation of the experiments is complicated by geometrical considerations and by absorption,[6] but it is clear that some of the neutrons are slowed down

TABLE III.

New activities produced by neutrons.

4	Be	^{6}He	0·9s	71, 95	57	La	1·9 d.	76
9	F	^{20}F	12 s.	95	58	Ce	—	
11	Na	^{20}F		95	59	Pr	19 h., 5 m.	
15	P	^{32}P	15 d.	96	60	Nd	1 h.	
17	Cl	^{35}S	80 d.	97	62	Sm	40 m., long.	
27	Co	^{59}Fe	72 h.	98	63	Eu	9·2 h.	
		^{60}Co	~ 1 yr.	13	64	Gd	8 h.	
28	Ni	$^{?}$Ni	3 h.	99	65	Tb	3·9 h.	
35	Br	Br	24 h.	1	66	Dy	2·5 h.	
39	Y	Y	70 h.	76	67	Ho	35 h.	
46	Pd	?	12 h., 3 m., 60 h.	2	68	Er	12 h., 7 m.	
50	Sn	Sn	0·8 m. ?, 18 m. ?	99, 3	70	Yb	3·5 h.	
					71	Lu	6 d., 4 h.	
					80	Hg	^{205}Hg 40 h.	4
					81	Tl	Tl 97 m., 4 m.	96
					90	Th	see p. 26.	
					92	U		

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[89] J. D. Cockcroft and E. T. S. Walton, *Proc. Roy. Soc.*, 1934, *A*, **144,** 704.

[90] M. L. Oliphant, A. E. Kempton, and (Lord) Rutherford, *ibid.*, 1935, *A*, **149,** 406.

[91] T. W. Bonner and W. M. Brubaker, *Physical Rev.*, 1935, **48,** 742.

[92] Oliphant, Kempton, and Rutherford, *Proc. Roy. Soc.*, 1935, *A*, **150,** 240.

[93] H. Miller, W. E. Duncanson, and A. N. May, *Proc. Camb. Phil. Soc.*, 1934, **30,** 549.

[94] J. Chadwick, N. Feather, and W. T. Davies, *ibid.*, 1935, **31,** 357; see also ref. 81.

[95] M. E. Nahmias and R. J. Walen, *Compt. rend.*, 1936, **203,** 71.

[96] P. Preiswerk and H. von Halban, *ibid.*, 1935, **201,** 722.

[97] E. B. Andersen, *Z. physikal. Chem.*, 1936, *B*, **32,** 237.

[98] *Idem, Nature,* 1936, **138,** 76.

[99] R. Naidu, *ibid.*, **137,** 578.

[1] C. H. Johnson and F. T. Hamblin, *ibid.*, **138,** 504.

[2] I. V. Kurtschatov, G. D. Lutischev, L. M. Nemenov, and I. P. Selinov, *Physikal. Z. Sovietunion,* 1936, **8,** 589.

[3] M. E. Nahmias, *Compt. rend.*, 1936, **202,** 1050.

[4] E. B. Andersen, *Nature,* 1936, **137,** 457.

[5] *Proc. Roy. Soc.*, 1936, *A*, **153,** 476.

[6] P. B. Moon, *Proc. Physical Soc.*, 1936, **48,** 648; J. R. Tillman, *ibid.*, p. 642; P. Lukirsky and T. Zarewa, *Nature,* 1936, **136,** 681; W. F. Libby and E. A. Long, *Physical Rev.*, 1936, **50,** 575.

to thermal values. This is confirmed by direct experiments.[7] Evidence has been obtained for the diffraction of slow neutrons at crystals, in accordance with the de Broglie wave-length of the neutrons.[8] An enormous mass of experimental material has been obtained on the scattering and absorption of the slow neutrons.[9] The scattering of neutrons by protons has been studied in order to check a theoretical formula of Wigner, but the results are not entirely consistent.[10]

TABLE IV.

Properties of slow neutrons.

(*a*) Groups of neutrons according to Fermi.[12]

	Strongly absorbed by	Activates		Strongly absorbed by	Activates
C	Cd		B	Ag (moderately)	Ag
D	Rh, In	Rh, In			
A	Ag	Ag, Ir	I	I	I

(*b*) Resonance energies for slow neutrons (from Rasetti, " Elements of Nuclear Physics," 1936, Blackie, London).

Element and period.	Resonance energy (volts).	Element and period.	Resonance energy (volts).
Rh 44 s.	1·1	In 54 m.	1·3
Rh 4 m.	$\sim$ 1	Ir 19 h.	$\sim$ 1·6
Ag 22 s.	2·5, 4·5	Au 2·7 d.	2·5
In 16 s.	$\sim$ 2		

The first theory of the capture of neutrons by nuclei [11] shows that in the absence of resonance the capture cross-section varies inversely with the neutron velocity. The experiments of P. B. Moon and

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[7] G. A. Fink, J. R. Dunning, G. B. Pegram, and D. P. Mitchell, *Physical Rev.*, 1936, **49**, 103.

[8] D. P. Mitchell and P. N. Powers, *Physical Rev.*, *ibid.*, **50**, 486; H. von Halban and P. Preiswerk, *Compt. rend.*, 1936, **203**, 73.

[9] C. H. Collie, *Nature*, 1936, **137**, 614; C. H. Collie and J. H. E. Griffiths, *Proc. Roy. Soc.*, 1936, *A*, **155**, 434; C. T. Zahn, E. L. Harrington, and S. Goudsmit, *Physical Rev.*, 1936, **50**, 570; D. P. Mitchell, *ibid.*, **49**, 453; G. A. Fink, J. R. Dunning, and G. B. Pegram, *ibid.*, **49**, 340; F. Rasetti, E. Segrè, G. A. Fink, J. R. Dunning, and G. B. Pegram, *ibid.*, p. 104; C. Y. Chao and C. Y. Fu, *Sci. Rep. Nat. Tsing Hua Univ.*, 1936, **3**, 451; I. Kara, L. Rosenkevitsch, C. Sinebrikov, and A. Walther, *Physikal. Z. Sovietunion*, 1935, **8**, 219; V. Fomin, F. G. Houtermans, J. V. Kurtschatov, A. I. Leipunski, L. Schubnikov, and G. Schtschepkin, *Nature*, 1936, **138**, 326; H. von Halban and P. Preiswerk, *ibid.*, **137**, 905; N. Dobrotin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **2**, 235; V. Fomin, F. G. Houtermans, A. I. Leipunski, L. B. Rusinov, and L. V. Schubnikov, *Nature*, 1936, **138**, 505; O. R. Frisch, G. Hevesy, and H. A. C. McKay, *ibid.*, **137**, 149; A. C. G. Mitchell, E. J. Murphy, and M. D. Whitaker, *Physical Rev.*, 1936, **50**, 133.

[10] M. A. Tuve and L. R. Hafstad, *ibid.*, p. 490; M. Goldhaber, *Nature*, 1936, **137**, 824.

[11] H. A. Bethe, *Physical Rev.*, 1935, **48**, 265; for other references, see *Ann. Reports*, 1935, **32**, 27.

J. R. Tillman[5] and of E. Fermi and E. Amaldi[12] show a selective effect, and Fermi divides neutrons into groups as in Table IV.

The neutrons of the C-group seem to have "thermal" velocities[13,14] with energies of the order 0·03—1·0 volt. The energies corresponding to the other bands have been determined[13, 14, 15] by assuming, on theoretical and experimental grounds,[14] that the capture of neutrons in boron and lithium (n; α transformation) follows the $1/v$ law. It being assumed that the capture process in cadmium takes place with maximum probability at about 0·03 volt, the energy for any other band can be determined from the absorption in boron or lithium. It appears that the resonances of rhodium, silver (22-s. period), indium, iridium, and gold lie in the range 1—5 volts, while manganese, copper, arsenic, bromine, silver (2·3 m.), iodine and rhenium are activated by higher-energy neutrons of 30—85 volts.

These phenomena have led to very interesting theoretical conclusions. N. Bohr[17] has given reasons for the existence of closely spaced energy levels in excited heavy nuclei, and he and G. Breit and E. Wigner[18] have shown that the assumption of such levels leads to a satisfactory explanation of slow neutron capture. The neutron entering the nucleus forms an excited compound nucleus, which breaks up with re-emission of a neutron scattering, or of another particle (n; p or n; α process), or goes into a lower state (capture). The existence of a number of closely spaced levels gives a possibility of resonance capture of a neutron at low energies. H. A. Bethe[19] calculates by a statistical argument that the spacing of the levels is of the order 50—500 V. for elements of medium atomic weight, while the excitation energy of the compound nucleus is of the order 10 M.E.V. The theory accounts for the fact[20] that good absorbers for slow neutrons are not always strong scatterers, the processes of capture and scattering being alternatives after the absorption has once taken place. Bohr[17] produces interesting arguments of a general kind to explain various features of the process. He suggests that the energy of capture is diffused inside the compound nucleus

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[12] *Ric. Sci.*, 1935, **2**, 344, 443; 1936, **1**, 56, 233, 310; L. Szilard, *Nature*, 1935, **136**, 950.

[13] H. H. Goldsmith and F. Rasetti, *Physical Rev.*, 1936, **50**, 328.

[14] O. R. Frisch and G. Placzek, *Nature*, 1936, **137**, 357.

[15] D. F. Weekes, M. S. Livingston, and H. A. Bethe, *Physical Rev.*, 1936, **49**, 471.

[16] F. Rasetti, D. P. Mitchell, G. A. Fink, and G. B. Pegram, *ibid.*, p. 777.

[17] *Nature*, 1936, **137**, 344.

[18] *Physical Rev.*, 1936, **49**, 519.

[19] *Ibid.*, **50**, 332.

[20] A. C. G. Mitchell and E. J. Murphy, *ibid.*, 1935, **47**, 881; **48**, 653; 1936, **49**, 400, 401; **50**, 133; see also ref. 76.

and finally becomes concentrated on an escaping particle. G. Gamow[21] has predicted resonances for the capture of fast neutrons by lighter nuclei to which the Bohr and the Breit–Wigner theory are inapplicable, but these have not yet been observed.

The production of γ-radiation attending the capture of slow neutrons has been studied by various workers,[22] and represents a method of studying nuclear excitation energies. S. Kikuchi, K. Husimi, and H. Hoki[23] find that the maximum γ-energy for a given element is connected with the atomic number by one of two smooth curves.

The β-*Disintegration.*—The conclusion that the upper limit of the continuous energy spectrum of β-particles represents the energy liberated in the nuclear reaction[24] has been strengthened by observations on the artificial β-ray emitters ^{12}B[56] and ^{13}N.[25] In both these cases the energy emitted in the β-ray change can be calculated independently, the energies of other reactions being used.

The β-ray and positron energy distributions from the radio-elements ^{13}N, ^{17}F, ^{24}Na, ^{31}Si, ^{32}P, Cl, ^{41}A, ^{42}K[26] and from indium, silver, rhodium, manganese, and dysprosium activated by neutrons[27] have been determined. The Konopinski–Uhlenbeck theory of the disintegration has been used in these experiments to provide an extrapolation formula for the observed energy distribution curves. The justification for this procedure is empirical. The relation between the maximum β-ray energy and the decay period of these lighter radioactive nuclei does not, apparently, show the regularity associated with the natural radio-elements (Sargent rules). The continuous β-spectra of some of the heavy radio-elements have been re-examined,[28] and the end-points determined with the aid of the Konopinski–Uhlenbeck formula. The values obtained for radium-*E* are not very concordant, but lie rather above the accepted value based on simple examination of distribution curves. The comparison of

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[21] *Physical Rev.*, 1936, **50**, 946.

[22] R. Fleischmann, *Z. Physik*, 1935, **97**, 242, 265; F. Rasetti, *ibid.*, p. 64; C. Haenny, *Compt. rend.*, 1936, **203**, 173; H. Herszfinkiel and L. Wertenstein, *Nature*, 1936, **137**, 106.

[23] *Ibid.*, pp. 186, 745, 992; see also *ibid.*, pp. 30, 398; cf. R. Fleischmann, *Naturwiss.*, 1936, **24**, 77.

[24] *Ann. Reports*, 1935, **32**, 32.

[25] W. A. Fowler, L. A. Delsasso, and C. C. Lauritsen, *Physical Rev.*, 1936, **49**, 561.

[26] F. N. D. Kurie, J. R. Richardson, and H. C. Paxton, *ibid.*, p. 369.

[27] E. R. Gaerthner, J. J. Turin, and H. R. Crane, *ibid.*, p. 793.

[28] F. A. Scott, *ibid.*, 1935, **48**, 391; F. C. Champion and N. S. Alexander, *Nature*, 1936, **137**, 744; P. C. Ho and H. Wang, *Chinese J. Physics*, 1936, **2**, 1; M. Lecoin, *Compt. rend.*, 1936, **202**, 1057; L. Goldstein and M. Lecoin, *ibid.*, p. 1169.

the form of the continuous β-spectrum of radium-*E* with that of ^{30}P[29] shows a considerable difference in the shapes of the curves, which is presumably connected with the difference between heavy and light nuclei.

There has been little development in the theory of the β-ray change. The current ideas of the continuous spectrum involve a non-ionising particle (neutrino) to carry away the energy difference between the energy of the nuclear reaction and that of the β-ray actually emitted from a particular nucleus. An attempt has been made to detect the neutrino by measuring the energy distribution of the nuclei recoiling after a β-ray change.[30] A light element, ^{11}C, was used so that the recoil velocity might be as high as possible. The experiment is difficult and the results rather indefinite, but they do favour the neutrino hypothesis. G. Gamow and E. Teller[31] have modified the Fermi theory as it refers to selection rules for the β-disintegration by taking into account the spin of the heavy particles in the nucleus. Their new selection rule is consistent with the observed lives of the different atoms of the thorium series. C. Møller[32] considers the possibility of the simultaneous creation of an electron–positron pair, together with the proton–electron pair of the Fermi theory. He uses this process to explain the positron emission observed by Alichanow, Alichanian, and Kosodaew from Th-*C* + ^{11}C. A theoretical calculation on the basis of the Fermi theory[33] shows that a weak continuous γ-ray spectrum should accompany the β-decay, especially in light elements. There is as yet no experimental evidence for this.

THE PASSAGE OF ENERGETIC β- AND γ-RAYS THROUGH MATTER.

The scattering of fast β-particles by nitrogen nuclei has been examined by F. C. Champion,[34] who finds general agreement with N. F. Mott's theoretical treatment, no losses of energy by radiation being found. D. Skobeltzyn and E. Stephanowa[35] find with β-rays of energy between 1·5 and 3 M.E.V. that there are sudden losses of energy when β-particles pass through nitrogen, which they ascribe to a special intranuclear effect. Similar collisions have been observed

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[29] A. I. Alichanow, A. I. Alichanian, and B. Z. Dželepov, *Nature*, 1936, **137**, 314.

[30] A. I. Leipunski, *Proc. Camb. Phil. Soc.*, 1936, **32**, 301.

[31] *Physical Rev.*, 1936, **49**, 895.

[32] *Nature*, 1936, **137**, 314.

[33] *Ibid.*, 1935, **136**, 475, 719; F. Bloch, *Physical Rev.*, 1936, **50**, 272; J. K. Knipp and G. E. Uhlenbeck, *Physica*, 1936, **3**, 425.

[34] *Proc. Roy. Soc.*, 1936, *A*, **153**, 353.

[35] *Nature*, 1936, **137**, 234, 456.

in argon.[36] Skobeltzyn and Stepanowa have also found evidence of electron–positron pair production by β-rays.[37] These developments must still be regarded as under investigation. Theoretical investigations of pair production by β-rays and protons have been made, which give a much lower order of magnitude for this effect.[38]

The production of pairs by γ-rays has been investigated theoretically [39] and experimentally.[40]

THE PENETRATING RADIATION.

The origin of the cosmic radiation remains obscure. Some further evidence has appeared against the reported increase in the radiation due to super-nova stars.[41] A. Ehmert [42] has reported that there is a diurnal change in the cosmic ray intensity. On account of the complicated paths followed by the particles in the earth's magnetic field, barometric changes which cause the rays to be filtered by more or less air have an effect on the phase of the diurnal variations which obscures the latter over long periods unless allowed for. This conclusion must for the present be accepted rather tentatively. The problems attacked by cosmic ray workers have been the nature of the primary particles and their behaviour in the earth's atmosphere and in other absorbers. The showers are especially interesting, both from the point of view of sub-atomic physics and in that they contribute to the radiation observed in the lower atmosphere. G. Pfotzer [43] has made balloon flights nearly to the top of the atmosphere with self-registering triple-coincidence sets of Geiger–Müller counters, and very recently R. A. Millikan, H. V. Neher, and S. K. Haynes [44] have sent electroscopes to comparable heights. Pfotzer's curve has as its main features a rise in the vertical intensity of the rays with altitude, a maximum at a barometric pressure of about 70 mm. of mercury, and a rapid fall at the top of the atmosphere. There is also a small subsidiary hump at about 300 mm. Pfotzer [45] has attempted a rather complete analysis of this curve, using the idea due to W. F. G.

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[36] L. Leprince-Ringuet, *Compt. rend.*, 1935, **201**, 712.

[37] *Nature*, 1936, **137**, 272.

[38] H. J. Bhabha, *Proc. Roy. Soc.*, 1935, *A*, **152**, 559; Y. Nishina, S. Tomonaga, and M. Kobayasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **27**, 137.

[39] J. C. Jaeger and H. R. Hulme, *Proc. Roy. Soc.*, 1936, *A*, **153**, 443.

[40] M. N. S. Immelman, *Naturwiss.*, 1936, **24**, 61; W. Bothe and H. Klarmann, *Z. Physik*, 1936, **101**, 489.

[41] J. Barnóthy and M. Forró, *Nature*, 1936, **138**, 544.

[42] *Z. Physik*, 1936, **101**, 260.

[43] *Ibid.*, **102**, 23.

[44] *Physical Rev.*, 1936, **50**, 992; cf. E. Regener and G. Pfotzer, *Physikal. Z.*, 1934, **35**, 782.

[45] *Z. Physik*, 1936, **102**, 41.

Swann[46] that primary particles come through a large part of the atmosphere, producing secondaries by the shower process with an efficiency increasing with the primary energy. The majority of the particles in the lower part of the atmosphere are secondary. The hump is due to the fact that below a certain altitude primary particles are being progressively removed as they come to the end of their range, while particles which would end above the critical altitude have been filtered out by the action of the earth's magnetic field. Pfotzer finds it necessary to postulate, in addition, a hard component which is absorbed exponentially and which he considers may be protons.[47] W. F. G. Swann[48] has produced independently a more complete and general but essentially similar theory. He finds it possible that the "hard component" is not affected by the earth's magnetic field, and may be due to photons. An unpublished argument by P. M. S. Blackett, based on a balance-sheet for the cosmic ray intensity entering the atmosphere, leads to the view that the number of particles entering the atmosphere is small compared with the number of secondaries formed and leaves place for an appreciable photon component. The existence of protons in the cosmic rays has been the subject of several investigations,[49] and it has been found that a few per cent. of the particles at sea level may be protons. If the hard component of the cosmic rays consists of protons, they must act as producers of secondaries.

P. M. S. Blackett and R. B. Brode[50] have obtained an energy distribution for the cosmic ray particles at sea level by measuring the curvature of their Wilson chamber tracks in the field of a large electro-magnet. The spectrum is approximately of the form $g(\mathrm{E}) = 1/E^2$ for energies between 2×10^9 and 2×10^{10} E. V. There is an irregularity in the spectrum at about $2{\cdot}5 \times 10^9$ E.V., which is probably significant and indicates a selective absorption action on particles of this energy, or possibly a singularity in the primary distribution.[51]

Several absorption measurements of the primary rays have been

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[46] *Physical Rev.*, 1935, **48**, 641; *Ann. Reports*, 1935, **32**, 37; cf. B. Gross, *Physikal. Z.*, 1936, **37**, 12.

[47] Cf. A. H. Compton, Guthrie Lecture, *Proc. Physical Soc.*, 1935, **47**, 747.

[48] *Physical Rev.*, 1936, **50**, 1103.

[49] C. G. Montgomery, D. D. Montgomery, W. E. Ramsey, and W. F. G. Swann, *ibid.*, p. 403; R. B. Brode, H. G. MacPherson, and M. A. Starr, *ibid.*, p. 383; W. F. G. Swann, *ibid.*, **49**, 478; T. R. Wilkins and H. St. Helens, *ibid.*, p. 403; L. H. Rumbaugh and G. L. Locher, *ibid.*, p. 885.

[50] *Proc. Roy. Soc.*, 1936, *A*, **154**, 564, 573; cf. L. Leprince-Ringuet, *Compt. rend.*, 1935, **201**, 1184.

[51] P. M. S. Blackett, unpublished.

made, showing hard and soft components.[52] The cosmic rays have been detected in a deep mine under the equivalent of 700 m. of water.[53] Evidence was found for the existence of showers at this depth. At a depth of 30 m. under London clay (60 m. water equivalent), D. H. Follett and J. D. Crawshaw [54] found that the proportion of showers to vertical rays was much the same as at sea level. The production of "showers" and "bursts" has been investigated with counter arrangements and with ionisation chambers. The experiments of H. Carmichael [55] show that even large bursts contain thinly ionising particles and are essentially identical with showers observed in the Wilson chamber or with counters. The production of very large bursts may occasionally be observed with a comparatively thin-walled steel chamber, so it is probable that showers start either in a single act or as a result of a cascade process with an enormous efficiency. The production of showers by electrons has been observed in the cloud chamber.[56] The evidence available shows that a rather large proportion of showers is initiated in this way.[56, 57] The efficiency of shower production, measured in thin layers of different elements, varies with the square of the atomic number.[58] This relation holds also at an altitude of 4000 m.[59] The average size of showers and bursts, as well as their frequency, increases with altitude.[60]

H. J. J. Braddick.

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[52] J. Clay, *Physica*, 1936, **3**, 332; P. Auger and A. Rosenberg, *Compt. rend.*, 1936, **202**, 1923.

[53] J. Barnóthy and M. Forró, *Nature*, 1936, **138**, 325, 399.

[54] *Proc. Roy. Soc.*, 1936, *A*, **155**, 546.

[55] *Ibid.*, **154**, 224; cf. W. Ehrenberg, *ibid.*, **155**, 532.

[56] E. C. Stevenson and J. C. Street, *Physical Rev.*, 1936, **49**, 425.

[57] J. Clay and A. Van Gemert, *Physica*, 1936, **3**, 763.

[58] C. G. Montgomery and D. D. Montgomery, *Physical Rev.*, 1936, **50**, 490; J. E. Morgan and W. M. Nielsen, *ibid.*, p. 882.

[59] Hu Chien Shan, unpublished.

[60] C. D. Anderson and S. Neddermeyer, *Physical Rev.*, 1936, **50**, 263; R. T. Young, *ibid.*, p. 638.

GENERAL AND PHYSICAL CHEMISTRY.

I. INTRODUCTION.

IN the present Report an attempt has been made to review some of the subjects which, on account of shortage of space, and for other reasons, were omitted from the previous Report. The application of quantum mechanics to the study of molecular structure and related problems has given important results but it has not been previously discussed adequately in the *Annual Reports* : this is no doubt to be attributed to the inherent difficulty of reviewing a subject of such complexity in the short space available. It may be noted, however, that a valuable survey of the quantum theory of valency has been made by J. H. Van Vleck and A. Sherman.[1] Spectroscopic methods continue to provide valuable information concerning molecular dimensions and valency force constants, and the article on spectroscopy in the present Report is a continuation of the previous one dealing with polyatomic molecules. The second volume of (Frl.) H. Sponer's book on Molecular Spectra [2] which was published during 1936, deals with a number of topics of special interest to chemists. Mention may also be made of the appearance of a comprehensive article on Raman spectra of organic compounds by J. H. Hibben,[3] and of a compilation of data of the Raman effect, covering the years 1931 to 1934, made by M. Magat.[4] Although the method of investigating molecular structure and inter-atomic distances by means of election diffraction in gases and vapours has been mentioned previously in these Reports, the subject has not been treated fully. An important review has appeared during the year by L. O. Brockway,[5] one of the chief workers in the field : this deals more particularly with the experimental method, and includes a comprehensive tabulation of the results obtained, with complete references, but the implications of the results are considered only briefly. In the present Report the emphasis is mainly on the significance of the measurements, although the principles involved in the interpretation of electron-diffraction photographs are also considered.

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[1] *Rev. Mod. Physics*, 1935, **7**, 167.

[2] " Molekülspektren," Vol. II, Springer, Leipzig, 1936.

[3] *Chem. Reviews*, 1936, **18**, 1.

[4] " Annual Tables of Constants and Numerical Data—The Raman Effect, 1931—4," Gauthier-Villars, Paris, 1936.

[5] *Rev. Mod. Physics*, 1936, **8**, 231.

Fundamental advances still continue to be made in the field of chemical kinetics, and the importance of the possibility of calculating the velocity of a chemical reaction from purely theoretical considerations of the molecules involved cannot be over-emphasised. It is inevitable, therefore, that there should again be a report on chemical kinetics.

In the Report for 1935 certain aspects of surface chemistry were discussed, and in the present Report two further aspects, *viz.*, colloidal electrolytes and unimolecular surface films, are reviewed. During the year the collected papers of Sir William B. Hardy [6] have been published, and a number of useful short monographs dealing with various topics in colloid and surface chemistry have been issued.[7] A very large number of measurements of dipole moments in solution have been described in recent years, and it is of importance to know how the values so obtained are related to the true values obtained from the temperature variation of the polarisation of the substance as vapour. Important progress has been made in this connexion and a report on the subject should not be out of place.

It will be observed that there is no special report on deuterium this year : there are several reasons for this omission, the chief being that the main interests of deuterium, namely, in spectroscopy and kinetics, are considered in the reports on these subjects. It is hoped, however, to review in a subsequent Report such properties of deuterium and of other isotopes as are not covered in this manner. Finally, it may be recorded that a report on photochemistry, for which the time is undoubtedly ripe, is in preparation and it is hoped to publish it next year. S. G.

2. The Quantum Mechanics of Molecules.

The interpretation of chemical binding offered by quantum mechanics has not been previously discussed in the *Annual Reports*, although J. H. Van Vleck and A. Sherman [1] have published a comprehensive review of the subject, including work to June 1935. The present Report is an attempt to combine a very brief survey of the whole field with an account of the main developments since this date.

The Report may be conveniently divided into sections, classified as follows :

(1) Variation methods for accurate calculations.
(2) Structural problems by approximate methods.

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[6] Collected Scientific Papers, Cambridge University Press, 1936.

[7] *Actualités Scientifiques*, Hermann, Paris.

[1] *Rev. Mod. Physics*, 1935, **7**, 167.

(3) Resonance and related properties.
(4) Interaction of atoms with solid surfaces.
(5) Miscellaneous.

Discussions on lattices and on activation energies and reaction rates are omitted, since the former topic has been dealt with very thoroughly in a recent book by N. F. Mott and H. Jones,[2] and the latter is dealt with later in this volume.[3]

(1) *Accurate Calculations by Variational Methods.*

Although quantum mechanics defines quite clearly a mathematical process by which the energy of formation of a molecule from atoms may be calculated, computational difficulties have prevented much progress from being made in all but the simplest cases. Two methods of approximation have been tried. The first is a generalisation of the Heitler-London theory of the hydrogen molecule. Molecular wave functions are constructed as the sum of products of atomic orbitals of the separate atoms, and the energy of formation of the molecule is evaluated as a first-order perturbation. This type of calculation has given many results of importance, but attempts to improve the numerical accuracy have led to many difficulties. The more obvious corrections, of which there are many, are relatively enormous, and it seems clear that the method cannot claim to have much more than qualitative significance. In spite of this, the application of the theory in its simplest form to the calculation of activation energies,[3] one reaction being calibrated in terms of another, has been remarkably successful. Because of this, the method is usually accepted as " semi-empirical."

The second possibility for calculating the energy of formation of a molecule makes use of the Ritz variation principle.[4] A promising form is selected for the approximate wave function of the ground state of the molecule, but the exact expression is left arbitrary to the extent of involving a number of parameters. The numerical values of these parameters are chosen in such a way that a certain integral, which is an approximation to the energy of the molecule, has its least value. The strength of this method lies in the fact that a first-order variation of the wave function from its true character causes only a second-order *increase* in the energy. The method therefore always gives a lower limit for the energy of formation.

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[2] " Properties of Metals," Oxford, 1936.

[3] P. 86.

[4] See, *e.g.*, ref. (1), or L. Pauling and E. B. Wilson, " Introduction to Quantum Mechanics," McGraw-Hill, 1935, Chapter XII.

At least half-a-dozen attempts have been made to calculate the energy of formation of the hydrogen molecule by a variation method.[4] Each succeeding author inserted more and more parameters into the wave function, thereby increasing the accuracy, but at the same time making the calculations much longer. Even so, the results were very disappointing until H. M. James and A. S. Coolidge [5] made a classical improvement. These authors demonstrated that it is absolutely essential to introduce the inter-electronic distance r_{12} explicitly into the wave function; otherwise, it is impossible to make proper allowance for the repulsion between the electrons. They assumed a 13-term expansion for the wave function, and adjusted each of the coefficients to give a minimum energy of formation. Their final result for the energy of dissociation, allowance being made for the residual energy,[6] was 4·454 ± 0·013 e.v., the accuracy being about the same as that obtainable by spectroscopic methods. H. M. James, A. S. Coolidge, and R. D. Present [7] have also considered the energy of the repulsive state of H_2 which dissociates into two normal hydrogen atoms. The same authors [8] then investigated the validity of the Franck–Condon principle by calculating the intensity throughout the continuous spectrum arising from transitions from an upper stable triplet level to the repulsive state. It appears that this principle leads to results incompatible with the experimental data. Which of the two is in error is not yet clear. J. K. Knipp [9] has made a 13-term expansion of the wave function of the ground state of lithium hydride, and has also considered the binding of the LiH^- ion. Both systems are stable, and in the case of the former the calculated energy is in fair agreement with experiment. The ion has so far not been observed experimentally. J. Y. Beach [10] has made a variation calculation on the ion HeH^+, and finds a dissociation energy of about 2·0 e.v. The doubly charged ion HeH^{++} is shown to be unstable. J. Hirschfelder, H. Eyring, and N. Rosen [11] have made a variation calculation on the energy of the linear H_3 molecule. They obtain 27 kg.-cals./mol. for the activation energy of the ortho–para hydrogen conversion, compared with the experimental value 7 kg.-cals./mol.[12]

[5] *J. Chem. Physics*, 1933, **1**, 825.

[6] C. G. Darwin (*Nature*, 1936, **138**, 908) makes the excellent suggestion that *residual energy* should be used instead of *zero-point energy*.

[7] *J. Chem. Physics*, 1936, **4**, 187.

[8] *Ibid.*, p. 193.

[9] *Ibid.*, p. 300.

[10] *Ibid.*, p. 353.

[11] *Ibid.*, p. 121.

[12] See, *e.g.*, A. Farkas, "Ortho-Hydrogen, Para-Hydrogen and Heavy Hydrogen," Cambridge University Press, 1935.

(2) *Structural Problems by Approximate Methods.*

Suppose that the energy of a molecule for all possible geometrical configurations can be calculated. Then the most stable arrangement is that where the energy function has its least value. Unfortunately, as explained in the previous section, at present it is impossible to make accurate calculations of the energy of formation of molecules other than the very simplest. Approximate methods must therefore in general be employed, and in practice there are two possibilities, known as the *orbital method* and the *pair method.* Both must be considered as limiting cases, and neither can claim always to be a better approximation than the other.

The orbital method attempts to solve separately the motion of each electron in the time–average potential field of the other particles of the system. Since an electron moves freely through the charge-density distribution representing the other electrons, the orbital method gives a finite probability that any two electrons will be at the *same place* at the *same time.* This is the main weakness of the orbital method, since, of course, the electrostatic repulsion e^2/r_{ij} between any two electrons i and j effectively prevents their ever simultaneously occupying the same spot.

The pair method attributes chemical binding to a number of bonds, each of which arises from the interaction of a pair of electrons on different atoms. Each bond is assumed similar in type to the Heitler–London bond of the hydrogen molecule. From the theory it appears that a necessary condition for a bond to be formed is that each electron entering into a bond should be in a singly occupied orbit of its atom (compare H + H and H + He; in the latter case there are two electrons in the same orbit, giving rise to *anti-bonding* or repulsion). The total energy of a molecule is the sum of the energies of the bonds, together with the sum of the interactions of electrons in different bonds. To make the energies of the bonds as large as possible, directed wave functions are employed, and it is from the mathematical construction of these wave functions that the spatial arrangement of the molecule is revealed.

The structures of a number of molecules and ions have been considered either by the pair method or by the orbital method. Of these we may mention water, methane, ethylene, ethane, hydrogen peroxide, hydrazine, benzene, and related systems, and $[Ni(CN)_4]^{2-}$ and other complex ions. Details will be found in the review article of J. H. Van Vleck and A. Sherman,[1] where references to the original papers are also given. As an illustration, however, we compare the view-points of the two methods on the ion $[Fe(CN)_6]^{4-}$.

The neutral iron atom has 26 electrons, of which all except two, the 3*d* electrons, are in closed shells. According to the pair theory, therefore, iron is at most bivalent. To possess a valency of *six*, the atom must acquire *four* more electrons, and these are provided in the ion. As shown by L. Pauling,[13] in order to construct six equivalent orbits, pointing to the corners of a regular octahedron, the six valency electrons of the central atom must have the aggregate configuration d^2sp^3. Moreover, only d orbitals of the symmetry type $d\varepsilon$ (of which there are three), and not orbitals of the symmetry type $d\gamma$ (of which there are two), must be used. The orbital theory also predicts the regular octahedral configuration, and uses only $d\varepsilon$, p, and s orbitals of the central atom. To this extent there is agreement between the two methods, but clearly the pair theory over-emphasises the capacity of the iron atom for absorbing electrons. On the other hand, the conventional structure $Fe^{++}(CN^-)_6$ goes too far in the other direction. Since, in the orbital theory there is no location of electrons on particular atoms, the "ionicity"[14] can assume a state intermediate between that of the pair model and that of the conventional model. For this reason the orbital method may be considered to give a better approximation than does the pair method for compounds involving iron-group atoms.

There has so far always been agreement between the predictions of the pair theory and those of the orbital theory for the forms of various specific molecules. Hitherto, this has been considered merely a fortunate circumstance, because it was felt that the approximations in the two methods were so drastic, and different, that sooner or later an example would be found where the methods seriously diverged. This rather worrying situation has to some extent been cleared up by J. H. Van Vleck.[15] His conclusions are so important that it is worth while summarising his arguments.

Consider a multivalent atom surrounded by a number of univalent atoms. According to the orbital theory, one constructs molecular orbitals of the form

$$\psi = \psi(C) + \Sigma_i a_i \psi_i,$$

where $\psi(C)$ is an atomic orbital of the central atom conforming to the symmetry of the whole molecule, ψ_i is the atomic orbital of the attached atom i, and a_i is a constant yet to be determined. Now, in general, there will be orbitals of the central atom whose symmetry types cannot be matched by linear combinations of the atomic

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[13] *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

[14] For want of a better word, we use "ionicity"; Mulliken uses "ionicness" and Van Vleck "ionic character." Distinguish between *ionic* and *polar*. Part of the bonding in H_2 is ionic because the molecule may have the instantaneous character $H^+ + H^-$, but the molecule is not polar because the ionic character averages out to zero.

[15] *J. Chem. Physics*, 1935, **3**, 803.

orbitals of the surrounding atoms, even though they obey the symmetry properties of the molecule. When this is so, the overlapping of the orbital of the central atom with that of the attached atoms will not be perfect, and anti-bonding, or at best weak bonding, results. Thus, in iron-group compounds with six univalent groups arranged octahedrally, the $d\varepsilon$ orbitals are bonding and the $d\gamma$ are not. Let us now consider the situation according to the pair theory. Here the object is to construct combinations of atomic orbitals of the central atom in such a way that each of the resulting wave functions is directed towards a particular attached atom. Hence these central directed wave functions have the same transformation properties as do those of the orbitals $\Sigma_i a_i \psi_i$ of the attached atoms in the orbital theory. As we have already explained, the orbital method requires only those orbitals of the central atom which are of the same symmetry types as linear combinations of orbitals of attached atoms. Therefore, the same atomic orbitals for the central atom must be used in the pair theory and in the orbital theory.

Van Vleck's paper contains further results of importance. From group-theory symmetry arguments he shows that if six atoms are attached either octahedrally or at the corners of a trigonal prism, only *s*, *p*, and *d* orbitals of the central atom are needed. Since these are commonly available, an immediate explanation of the frequent appearance of co-ordination numbers six is obtained. On the other hand, if eight atoms are attached to the central atom their full bonding power is not used unless *f* wave functions of the central atom are included. As a rule *f* orbits are considerably higher in energy than *d*, *p*, or *s* orbits, but this is no longer true for very heavy elements. Prior to Van Vleck's paper, J. E. Lennard-Jones [16] had suggested that only very heavy elements could have a valency of eight, and quoted OsO_4 as an example. The atoms in the neighbourhood of osmium in the periodic table are the first where the outermost electrons can be easily changed from *s* to *f* orbits.

Mulliken's Papers.—R. S. Mulliken,[17] in a formidable series of papers extending over several years, has made an intensive study of the molecular orbitals, ionisation potentials, dipole moments, and electron affinities of a number of triatomic, tetra-atomic, and even more complicated molecules. Most of his papers are mainly concerned with the spectroscopy of polyatomic molecules and are therefore hardly appropriate for review here.

Paper VIII deals with the effect of dipoles in the molecule on the

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[16] *J. Soc. Chem. Ind.*, 1934, **53**, 249.

[17] VIII, *J. Chem. Physics*, 1935, **3**, 514; IX, *ibid.*, p. 518; X, *ibid.*, p. 564; XI, *ibid.*, p. 579; XII, *ibid.*, p. 586; XIII, *ibid.*, p. 635; XIV, *ibid.*, p. 720.

ionisation potential. W. C. Price [18] has shown experimentally that an effect of this type is present in methyl iodide.

Paper IX enumerates the one-electron molecular orbitals of methane, ethane, ethylene, and acetylene. By considering the ultra-violet absorption spectra and the ionisation potentials of these molecules, fairly precise estimates of the bonding powers of the various orbitals are obtained. Similar considerations for aldehydes, ketones, and related molecules are given in Paper X.

Papers XI and XII consider the molecular orbitals of molecules which are appreciably polar, and supply a rough theoretical justification of L. Pauling's electronegative scale for atoms.[19] From Pauling's values, the polarity of molecules can be estimated; for example, Mulliken finds, very roughly, $C^{-0\cdot72}(H^{0\cdot18})_4$ for methane and $C^{0\cdot60}(Cl^{-0\cdot15})_4$ for carbon tetrachloride.

Paper XIII deals with the molecular orbitals in diborane. The experimental fact that this compound is diamagnetic at room temperatures [20] requires a singlet for the ground state. Previously, it was thought that a triplet state might be lowest.[21]

Paper XIV is concerned with "isosteres." I. Langmuir [22] introduced this term to denote molecules having the same number of electrons and the same electronic structure as judged by their properties; *e.g.*, nitrogen and carbon monoxide, nitrous oxide and carbon dioxide. Mulliken considers 15 isosteres of the last and discusses their molecular orbitals, "ionicity," ionisation potentials, and ultra-violet spectra. As a rule, molecules containing the same number of electrons, and whose nuclei correspond closely in nuclear charge, have the same shape and similar physical properties. This rule has been verified by W. G. Penney and G. B. B. M. Sutherland [23] in the case of a number of triatomic systems.

Valency States of Carbon.—A type of calculation where the pair method has so far proved more fruitful than the orbital method is in estimating the energy of valency states of atoms. By far the most interesting case from a practical point of view is, of course, carbon. The first explicit calculation of the energy of the valency state of carbon was given by J. H. Van Vleck [24] on the assumption of an aggregate sp^3 configuration. For any particular arrangement of the four bonds, the valency state involves to a varying extent the various states of the free atom in the sp^3 configuration (*viz.*,

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[18] *J. Chem. Physics*, 1936, **4**, 539.

[19] *J. Amer. Chem. Soc.*, 1932, **54**, 3570.

[20] L. Farkas and H. Sachsse, *Trans. Faraday Soc.*, 1934, **30**, 331.

[21] R. S. Mulliken, *Physical Rev.*, 1933, **43**, 765.

[22] *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543.

[23] *Proc. Roy. Soc.*, 1936, *A*, **156**, 654.

[24] *J. Chem. Physics*, 1934, **2**, 20, 297.

$^{5.3}S$, $^{3.1}D$, $^{3.1}P$), and the energy of the valency state is easily evaluated by the pair method in terms of these states. The results were 163 kg.-cals./mol. for the energy in the tetrahedral arrangement (*e.g.*, as in methane, ethane, etc.), and 167 kg.-cals./mol. for the trigonal arrangement (*e.g.*, as in ethylene, benzene, etc.). The difference is practically without significance.

H. H. Voge[25] has improved on the above estimate. He assumes that the valency state is a mixture of sp^3 and s^2p^2, and adjusts the " coefficient of mixing " in such a way that the energy of methane as calculated by the pair method is a minimum. He concludes that the valency configuration is mainly sp^3 and that the energy of the valency state is about 106 kg.-cals./mol., a figure appreciably lower than Van Vleck's estimate. However, the gross bonding energy is also affected, and the net calculated heat of formation of methane is increased by only 28 kg.-cals./mol.

Voge assumes from the experimental evidence that the heat of formation of methane from atoms is 390 kg.-cals./mol. This enables him to fix certain parameters which are then used to calculate the heats of formation of CH, CH_2, and CH_3. He finds 92, 194, and 278 kg.-cals./mol. respectively. There is no indication that CH_2 occupies a favourable position with respect to the others. The most stable arrangement of CH_3 is planar, in agreement with earlier calculations.[26] No attempt was made to calculate the energy of formation of CH_5.

(3) *Resonance.*

The word resonance is being used in many different senses in the theory of the structure of molecules. We shall follow Pauling and his collaborators[27] and say that " resonance " is present in any system which cannot be adequately described in terms of a single bond diagram. The choice of the term is hardly a happy one because the connexion between " resonance " in the present sense and resonance in the ordinary mechanical sense is rather remote. The word, however, was introduced before the precise nature of the effect was understood, and the mechanical analogy did at least offer a plausible interpretation of the experimental facts. In any case, the word is now so commonly used that it would be a mistake to attempt to substitute another. A better word, " mesomerism," has indeed been suggested by C. K. Ingold,[28] and this fits in well with

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[25] *J. Chem. Physics*, 1936, **4**, 581.

[26] J. H. Van Vleck, *ibid.*, 1934, **2**, 20; W. G. Penney, *Trans. Faraday Soc.*, 1935, **31**, 734.

[27] L. Pauling and G. W. Wheland, *J. Chem. Physics*, 1933, **1**, 362, and many subsequent papers.

[28] *Nature*, 1934, **133**, 946.

all the other " merisms " of chemistry. From the construction of the word mesomerism, a situation is implied where the actual conditions are intermediate between various extremes.

The mathematical calculations of the theory of resonance have achieved two results of importance. These are best illustrated by reference to benzene. The main result is that all of the bonds between neighbouring carbon atoms are similar, and are intermediate between single and double bonds. Hence all carbon atoms are equivalent, and the chemical stability (*i.e.*, reactions with acids, etc.) is greater than would be expected if the molecule contained three localised double bonds. The second result is that the effect of resonance is to increase the mechanical stability (*i.e.*, the energy of formation from atoms) beyond that expected on the hypothesis of a single bond structure. The increase is not very much compared with the energy of formation of the molecule (in benzene, for example, about 2 e.v. in 60 e.v.), but it is quite enough to be detected in the ordinary calculations of heats of formation in terms of bond energies.

It is noteworthy that the first of these results cannot be upset by improving the accuracy of the calculations, but that the second may be. This, it seems to us, is an important point not explicitly mentioned before. One of the most surprising features of the long series of calculations made by Pauling and his collaborators on the increase of mechanical stability of a molecule due to resonance is that the results are so remarkably consistent. No doubt it is an example of a simple theory which concentrates on an essential point giving results with an accuracy very difficult to obtain by more complicated theories, because in these the second, third, and higher approximations, although all large, practically balance out to zero.

Effect of Resonance on Internuclear Distances.—It is well known that internuclear distances in molecules are affected by resonance. For example, the carbon–carbon distance in benzene is 1·39 A.,[29] intermediate between the single-bond value 1·54 A.[30] and the double-bond value 1·33 A.[31] L. Pauling, L. O. Brockway, and J. Y. Beach [32] have suggested a method of estimating internuclear distances affected by resonance. We may illustrate their suggestion by considering the benzene molecule. Here the resonance is mainly between the two Kekulé structures. Since neighbouring carbon

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[29] L. Pauling and L. O. Brockway, *J. Chem. Physics*, 1934, **2**, 867.

[30] See, *e.g.*, Sidgwick, " The Electronic Theory of Valency," Oxford, 1927.

[31] Pauling, Brockway, and Beach use 1·37 A. As will be shown by one of the Reporters in an article soon to appear in the *Proc. Roy. Soc.*, the value 1·33 is probably the correct one.

[32] *J. Amer. Chem. Soc.*, 1935, **57**, 2705.

atoms linked by a single bond in one structure are linked by a double bond in the other, the carbon–carbon linkage may be said to be of order 3/2. Considerations of a similar sort [33] show the linkage in graphite to be of order 4/3, while the internuclear distance is known accurately to be 1·41 A.[34] Thus four simultaneous pairs of values of internuclear distance and bond order are known. By plotting order against distance a smooth curve results. This curve may be used to predict distances in molecules where it is possible to estimate the bond order. To find the order of the linkages in any molecule, Pauling, Brockway, and Beach proceed as follows. The resonance problem is solved by the pair method, and the wave function of the ground state is obtained in the form

$$\Psi = \Sigma_j k_j \psi_j$$

where k_j is a numerical constant, and ψ_j is the wave function corresponding to the canonical structure j. The order of the linkage p between neighbouring carbon atoms is then defined as

$$p = \Sigma_j g_j (k_j)^2 / \Sigma_j (k_j)^2,$$

where g_j is unity if the canonical structure j has a bond between the two atoms, and is zero otherwise.

By substituting for naphthalene the values of the coefficients k_j as calculated by L. Pauling and J. Sherman,[35] it is found that the linkages are not all equivalent. Variations of some 0·06 A. about the mean 1·41 A. are to be expected. J. M. Robertson [36] finds a mean internuclear distance 1·41 A., in exact agreement with this. No attempt has so far been made to measure deviations from the mean.

Pauling, Brockway, and Beach suggest that the curve relating internuclear distance with bond order which they obtain for carbon compounds may be used for molecules containing other elements provided a suitable change of scale and end-points is made. Alternatively, if an internuclear distance is known from experimental data, then, by using Pauling's values of single-, double-, and triple-bond ionic radii,[37] the order of the linkage may be calculated. In this way, *e.g.*, the carbon–chlorine bond in carbonyl chloride is calculated as 83% single and 17% double bond. Many other examples are considered.

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[33] J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1934, **30**, 58; G. W. Wheland, *J. Chem. Physics*, 1934, **2**, 474.

[34] G. I. Finch and H. Wilman, *Proc. Roy. Soc.*, 1936, *A*, **155**, 345.

[35] *J. Chem. Physics*, 1933, **1**, 679; *ibid.*, 1934, **2**, 488.

[36] *Proc. Roy. Soc.*, 1933, *A*, **142**, 674.

[37] *Proc. Nat. Acad. Sci.*, 1932, **18**, 293.

(4) *Interaction of Atoms with Solid Surfaces.*

Lennard-Jones and his collaborators[38] have made an extremely promising start at a detailed theory of the interaction of atoms and molecules with the surfaces of crystals. The type of system which they consider is one where the absorbed atom is held only loosely by the crystal, probably by forces of a van der Waals character. The atom can exist in one of a small number of vibrational levels or, if its energy is great enough, can leave the surface altogether. Questions which are studied are the spacing of the energy levels, transitions between them, and between them and the continuum, caused by the thermal agitation of the surface, the migration of the atom over the surface, and the scattering of a homogeneous beam of the atoms by the crystal.

The fundamental approximation of the theory is that the energy of interaction of the absorbed atom and the crystal may be represented by a Morse function.[39] Let the z axis be drawn through the absorbed atom, perpendicular to the surface of the crystal. Write Z for the displacement at a particular instant of the surface atoms of the crystal in the neighbourhood of the absorbed atom from their mean position $Z = 0$, and z for the displacement of the absorbed atom from $Z = 0$ at the same instant. Let b be the equilibrium distance of the absorbed atom from the surface at the absolute zero of temperature. Then the interaction energy of the absorbed atom with the crystal is written

$$V = De^{-2\kappa(z-b-Z)} - 2De^{-\kappa(z-b-Z)}$$

The first of these terms represents the short-range repulsive field, and the second the long-range attractive field. The constant D is the energy required to take the atom off the surface at absolute zero, and κ is a parameter controlling the breadth of the potential trough holding the atom on the surface.

The motion of the surface atoms of the crystal is small compared with the range of the potential field V. Hence V may be expanded in a power series in Z, and terms after the second rejected. We then obtain

$$V = V_0 + V_1 = [De^{-2\kappa(z-b)} - 2De^{-\kappa(z-b)}] + 2\kappa DZ[e^{-2\kappa(z-b)} - e^{-\kappa(z-b)}]$$

The first term gives the interaction energy of the atom and crystal

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[38] I, J. E. Lennard-Jones and C. Strachan, *Proc. Roy. Soc.*, 1935, *A*, **150**, 442; II, C. Strachan, *ibid.*, p. 456; III, J. E. Lennard-Jones and A. F. Devonshire, *ibid.*, 1936, *A*, **156**, 6; IV, *idem*, *ibid.*, p. 29; V, A. F. Devonshire, *ibid.*, p. 37; J. E. Lennard-Jones and A. F. Devonshire, *Nature*, 1936, **137**, 1069.

[39] See, *e.g.*, L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill, 1935, p. 271.

at absolute zero, and the second gives the coupling between the vibrations of the attached atom in the field of the stationary surface, and the thermal vibrations of the lattice. The effect of V_1 is to cause a surge of energy to and fro between the crystal and the attached atom.

An important step has now been made. The perturbing potential V_1 and the complete wave functions of the system are all in product form, one factor of each depending only on the lattice, and the other depending only on the attached atom. Straightforward perturbation technique may be applied, and there results the probability that the lattice loses to the atom just the right amount of energy needed to cause excitation to a higher vibrational level. This process may occur in many ways, because of the large number of degrees of freedom of the lattice. An averaging process over all the normal modes present at any temperature must therefore be made, and at this point temperature appears explicitly in the formulæ. The final result of paper I is the life-time of the attached atom in a vibrational level on the surface. For argon on potassium chloride at low temperatures, the atom vibrates many times in the ground state before being activated to the first excited state, while at room temperatures the interval is of the same order as the vibration period.

Paper II extends the above calculations to transitions of the absorbed atom from a discrete state to the continuum. By integrating over the continuum, an expression is obtained for the probability of evaporation from the surface. The average length of time spent by an absorbed atom on a surface may thus be estimated as a function of temperature.

Paper III extends the calculations of paper II. Formulæ are found for the probability that an impinging particle will condense on a solid surface. The constants which occur in Langmuir's isotherm are thus for the first time explicitly calculated in terms of the physical properties of the solid and its surface field. Evaporation processes are also considered. It is found that evaporation may, even at low temperatures, take place in two or more stages, the atom being first excited to a higher vibrational level and then, while in that excited state, receiving another quantum of energy sufficient to cause evaporation. The theory is illustrated by considering the condensation and evaporation of H_2, HD, and D_2 on the same solid surface.

Paper IV covers roughly the same ground as paper III. This time the potential holding the atom on the surface is assumed to have central symmetry about the point of attachment.

Paper V gives an interpretation of the experiments of R. Frisch and O. Stern[40] on the scattering of beams of helium by crystals of lithium fluoride and sodium fluoride. The theory shows that when the components of momenta of the incident beam satisfy certain relations, involving the energy intervals of the vibration spectrum of the atom on the crystal, absorption without loss of energy can occur, thus accounting for minima in the reflected and refracted beams. Excellent agreement with experiment is obtained if it is assumed that helium on lithium fluoride can exist in two vibrational levels, given by − 129 cals./mol. and − 57 cals./mol. severally. Similar values hold for helium on sodium fluoride, but here the exact figures are somewhat doubtful because the experiments were not so complete.

(5) *Miscellaneous.*

A number of papers have recently appeared dealing with the theory of various physical properties of molecules and crystals. For want of space, these are grouped together under this heading.

Restricted Rotation.—To account for the temperature variation of the specific heat of certain crystals (*e.g.*, oxygen, nitrogen, iodine, methane, carbon dioxide, etc.), L. Pauling suggested in a classical paper[41] that above a critical temperature, depending on the crystal, the molecules rotate more or less freely, but that at lower temperatures rotation is inhibited and only oscillation occurs. Each molecule is supposed to be influenced by an inhomogeneous potential field due to the surrounding molecules. When the mean thermal energy, as measured by kT, is small compared with the restricting potential, most of the molecules have not enough energy to turn over, and their motion is therefore mainly oscillatory. At high temperatures, however, the mean thermal energy is more than enough to overcome the restricting potential, and rotation is common throughout the crystal. According to these ideas, the specific heat of the crystal should show a maximum at temperatures where kT is about equal in magnitude to the restricting potential. By observing where the maximum occurs, a rough estimate of the restricting potential may be obtained.

The above theory is unable to account for a maximum in the specific heat–temperature curve of anything like the magnitude and sharpness of that observed. R. H. Fowler[42] has explained the reason. It is because the restricting potential acting on one molecule depends on whether the other molecules near it are also rotating. By making the magnitude of the restricting potential a function of the amount of rotation already present in the crystal, the specific

[40] *Z. Physik*, 1933, **84**, 430.

[41] *Physical Rev.*, 1930, **36**, 430.

[42] *Proc. Roy. Soc.*, 1935, *A*, **151**, 1.

heat curve can be made to follow the experimental results very closely. Similar calculations on the dielectric constants along the three principal axes of susceptibility of certain crystals also give good agreement with the somewhat peculiar observed results.[43]

Suppose that the restricting potential on one molecule due to the rest of the crystal is expanded in a Taylor's series about the centre of the molecule. Apart from an additive constant which does not affect the freedom of rotation, the potential V may be written

$$V = (Ax^2 + By^2 + Cz^2) + (Dx^3 + \ldots) + \ldots \quad . \quad . \quad (1)$$

Since V is a potential in a region due to outside charge distributions, the terms of each order in V must satisfy Laplace's equation. Assume now that the molecules are arranged in the lattice with cubic symmetry. Then the first non-vanishing terms in V are those of fourth order, and they may be written

$$V = k\{3r^4 - 5(x^4 + y^4 + z^4)\} . \quad . \quad . \quad . \quad (2)$$

A. F. Devonshire[44] has investigated the effect of the potential field [equation (2)] on the energy levels of the dumb-bell rotator. The way in which the various rotational levels, characterised by the rotational quantum number J, split up under the influence of the field had already been worked out by H. Bethe[45] from the methods of group theory. The levels belong to five different symmetry types (irreducible representations), and therefore the infinite secular equation giving the energy levels of the system factorises into five equations, each of which is infinite and refers to one of the representations. Devonshire confined his attention to the first few rows and columns of each determinant, and obtained the approximate roots with the aid of an electrical calculating machine.[46] The calculations were straightforward for the levels up to about $J = 5$ and $|k|$ not too large. Special considerations were needed for $|k|$ large, and the asymptotic behaviour of the levels was considered. Curves showing the behaviour of the energy levels as $\overline{kr_4}$ ranges from -60 to $+60$ are given in the paper. The notation used to describe the levels is that suggested by R. S. Mulliken.[47] Whether there is any molecular crystal to which the theory worked out by Devonshire would apply has not yet been considered. The interpretation of the experimental results will in any case be very difficult, because the crystalline forces will probably break down most of the ordinary selection rules, and levels considerably higher than $J = 5$ will be present even at low temperatures.

[43] R. H. Fowler, *Proc. Roy. Soc.*, 1935, *A*, **149**, 1.

[44] *Ibid.*, 1936, *A*, **153**, 601.

[45] *Ann. Physik*, 1933, **3**, 133.

[46] R. R. M. Mallock, *Proc. Roy. Soc.*, 1932, *A*, **140**, 457.

[47] *Physical Rev.*, 1933, **43**, 278.

Paramagnetic Properties of Crystals.—There is a very close formal connexion between the calculations of the previous section and those giving the paramagnetic properties of crystals of iron-group and rare-earth salts. The paramagnetism arises from the presence in the metallic ion of electrons in incomplete shells to a large extent unaffected by the crystalline forces. For this reason, the crystalline potential acting on an ion may be expanded in a Taylor's series similar to (1). If the atoms surrounding the ion have cubic symmetry, then once again we have the potential (2). Now very often the atoms surrounding the ion are arranged with cubic symmetry, and therefore the study of the effect of the field (2) on the energy levels of paramagnetic ions is of real practical importance. The theory in the case of hydrated crystals has already been carried to the point of accurate quantitative agreement with experiment,[48] but in the case of certain complex salts, notably ferro- and ferricyanides, and cobaltammines, the theory is not so well developed. These salts are diamagnetic if they involve a complex ion containing an even number of electrons, *e.g.*, $[Fe(CN)_6]^{4-}$, and have a susceptibility of order of magnitude corresponding to one free spin if this number is odd, *e.g.*, $[Fe(CN)_6]^{3-}$. L. Pauling [13] was the first to account for this behaviour, but his explanation was not entirely satisfactory because it was based on directed wave functions and perfect electron pairing. J. H. Van Vleck [49] has now put the matter on a much wider foundation. He shows that the method of crystalline fields, as outlined above, the method of electron pairs, and the method of molecular orbitals all formally predict similar results. The crystalline forces are so strong that the Russell–Saunders coupling is broken down and the state of lowest energy is one of lowest possible spin for the whole complex ion, rather than one in which the central metallic ion has its greatest allowed spin. In other words, the complex ion must be considered as a unit in which the interactions between electrons in orbits of the metallic ion are of subsidiary importance to interactions between these electrons and the electrons of the surrounding co-ordinated systems.

J. B. Howard [50] has made detailed numerical calculations on the principal magnetic susceptibilities of potassium ferricyanide by the method of crystalline potentials. His results confirm the above theory of Pauling and Van Vleck.

Diamagnetic Anisotropy of Aromatic Molecules.—When the structure of a molecule may be represented by a single bond diagram,

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[48] See, *e.g.*, a review article by R. Schlapp and W. G. Penney, "Reports on Progress in Physics," II, 1935, Physical Society, p. 60.

[49] *J. Chem. Physics*, 1935, **3**, 807.

[50] *Ibid.*, p. 813.

the diamagnetic susceptibility may be calculated by adding together the susceptibilities of the separate atoms of the molecule.[51] This is because the susceptibility of a free atom is proportional to $\Sigma\overline{r^2}$, where $\overline{r^2}$ is the mean square radius of an electron's orbit, and the sum is over all the electrons of the atom. If resonance occurs in the molecule, however, the situation is different. Consider the benzene molecule, for example. Here, the electrons concerned in bonds in the plane of the ring, *i.e.*, those whose atomic orbitals are symmetrical about the plane of the ring, are regular, and for these the additive principle applies. The resonance electrons have a charge distribution which is practically cylindrically symmetrical about the axis of the molecule, and is large only in two anchor-ring regions, one above and one below the carbon hexagon. When the magnetic field is parallel to the plane of the molecule, the contribution to the susceptibility is normal, because the mean square distance of the anchor rings above or below the central plane is about the same as $\overline{r^2}$ for a p orbit of carbon. When the magnetic field is perpendicular to the plane of the molecule, on the other hand, the contribution to the susceptibility is not normal, as it is proportional to R^2, where R is the radius of either anchor-ring region, and is also approximately the C–C distance in the ring (since the side of a regular hexagon equals the radius of the circumscribing circle). Now, R^2 is several times larger than $\overline{r^2}$ for a p orbit of carbon, and the susceptibility of benzene in a direction perpendicular to the plane of the molecule is therefore much greater than that in a direction parallel to this plane.

L. Pauling[52] has estimated the principal diamagnetic susceptibilities of a number of aromatic molecules, using the above ideas as a basis. He finds almost exact agreement with experiment in the case of benzene. More complex molecules he calibrates very ingeniously in terms of benzene, and for these, too, obtains excellent agreement with experiment. The method of calibration is to replace any pair of neighbouring electrons in the resonance problem by a constant electrical resistance. A conducting network is then obtained, and the currents induced in this network when a time-varying magnetic field acts in a direction perpendicular to the plane of the network, and hence the magnetic moment of the network, are found in terms of those corresponding to benzene. The contributions of the resonance electrons of the molecules to the magnetic susceptibility are linearly proportional to the magnetic moments of the networks. For naphthalene and anthracene the calculated and the observed values do not agree so well as do those of other

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[51] See, *e.g.*, E. Stoner, "Magnetism and Matter," Methuen, 1934, p. 469.

[52] *J. Chem. Physics*, 1936, **4**, 673.

molecules. Pauling therefore considers that the experimental results for these molecules are probably in error.

Vibrational and Rotational Levels of Polyatomic Molecules.—The calculation of the vibrational and rotational levels, and their statistical weights, has an important bearing on specific heats. However, the subject is more appropriately dealt with in the theory of infra-red spectra and will therefore not be considered here. An adequate review of the subject, treated by the methods of group theory, has recently been given by J. E. Rosenthal and G. M. Murphy.[53]

W. G. P.
G. J. K.

3. SPECTROSCOPY.

In this section of last year's Reports a general review was given of the various types of vibration spectra associated with polyatomic molecules; the information derivable from them was indicated, and its limitations considered, but little attention was paid to particular instances. This year it is proposed to exemplify the more important results by a small compilation. We shall follow the classification of molecules given in last year's Reports, *viz.*, linear molecules, spherical molecules, symmetrical-top molecules, and asymmetrical-top molecules. The examples we have taken in each class are the only ones for which the moments of inertia have been determined with any degree of certainty from the rotational fine structure of the bands. The methods of finding molecular dimensions from vibrational frequencies alone cannot yet be regarded as giving precision values: these methods will be discussed later in this Report. It will be observed that several molecules have been listed containing the deuterium isotope; in all of these cases it has been assumed that the dimensions are exactly the same as for the molecule containing the corresponding hydrogen atom; in fact, this assumption has occasionally made it possible to determine the dimensions. The inaccuracy from this cause cannot be more than about 0·001 A. in an internuclear distance. The values of the fundamental frequencies of the molecules have only been given to within 10cm.$^{-1}$, since corrections have not been made for anharmonicity, and accordingly these values may be in error by approximately that amount. The figure in parentheses after certain of the frequencies indicates the degree of degeneracy for frequencies which are isotropic in two (2) or in three (3) dimensions. Data which are not connected to a specific reference number have been taken from H. Sponer's compilation.[1] Paren-

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[53] *Rev. Mod. Physics*, 1936, **8**, 317.

[1] "Molekülspektren," Springer, 1935.

theses placed round a frequency indicate that the value is a calculated one, included for completeness, and probably correct to within 30 $cm.^{-1}$.

TABLE I.

Linear Molecules.

Molecule.	Internuclear distance, A.	Moment of inertia, g.-cm. × 10^{40}.	Fundamental frequencies, $cm.^{-1}$.
OCO	CO 1·16	70·6	2360
			1320
			670 (2)
SCS	CS 1·52[2]	247[2]	1520
			660
			400 (2)
NNO	—	66	2220
			1290
			590 (2)
HCN	CH 1·06[3]	18·7[3]	3290
	CN 1·15		2090
			712 (2)
DCN	CD 1·06[3]	22·9[3]	2630
	CN 1·15		1900
			570 (2)
HC⋮CH	CH 1·057[4]	23·5	3290
	CC 1·204		3370
			1980
			730 (2)
			610 (2)
HC⋮CD	CH 1·057[4]	27·9[4]	2590[4, 5]
	CD 1·057		3380
	CC 1·204		1880
			680 (2)
			520 (2)
DC⋮CD	CD 1·057[4]		(2410)[4, 5]
	CC 1·204		2700
			1760
			540 (2)
			500 (2)

In addition to those in Table I, the following molecules and ions have been shown to be linear and have had their vibration frequencies determined; their actual dimensions, although not determined spectroscopically, are known in many cases from studies on *X*-ray or electron-diffraction (see p. 65): carbonyl sulphide,[1] cyanogen chloride,[1] cyanogen bromide,[1] cyanogen iodide,[1] cyanogen,[6] C_4H_2,[1] N_3^-,[7] SCN^-.[1]

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[2] J. A. Sanderson, *Physical Rev.*, 1936, **50,** 209.

[3] P. F. Bartunek and E. F. Barker, *ibid.*, 1935, **48,** 516.

[4] G. Herzberg, F. Patat, and J. W. T. Spinks, *Z. Physik*, 1934, **92,** 87; G. Herzberg, F. Patat, and H. Verleger, *ibid.*, 1936, **102,** 1.

[5] W. F. Colby, *Physical Rev.*, 1935, **47,** 388; G. Glockler and C. E. Morrell, *ibid.*, p. 569.

[6] S. C. Woo, T. K. Liu, and T. C. Chu, *J. Chinese Chem. Soc.*, 1935, **3,** 301.

[7] W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156,** 654.

In the case of carbon dioxide the value given for one of the frequencies as 1320 cm.$^{-1}$ requires further explanation. Actually, one observes no frequency of this magnitude, but a pair of frequencies at 1286 cm.$^{-1}$ and 1388 cm.$^{-1}$. This arises because the overtone of the frequency at 670 cm.$^{-1}$ falls very close to this fundamental, so causing a " resonance " splitting.[8] The value given is therefore an estimate of the unperturbed frequency and is sufficiently good for most calculations. The frequency at 660 cm.$^{-1}$ for carbon disulphide is probably slightly erroneous for the same reason.

In addition to those in Table II, the following molecules and ions have been shown to be spherical; their vibration frequencies are known and their dimensions have been deduced in many cases from data on *X*-ray and electron diffraction (see p. 65) : carbon tetrabromide,[1] silicon tetrachloride,[1] titanic chloride,[1] stannic chloride,[1] stannic bromide,[1] SO_4'',[18] ClO_4'[18]. It will be noticed that three values

TABLE II.

Spherical Molecules.

CH_4	CH	1·09 [9]	5·298 [9]	2910
	HH	1·785	5·47 [10]	3020 (3)
			5·27 [11]	1520 (2)
				1300 (3)
CD_4	CD	1·09 [9]	10·91 [12]	2080 [13, 14]
	DD	1·785		2260 (3)
				(1070)(2)
				990 (3)
GeH_4 [15]	GeH	1·37	7·0	1990
	HH	2·06		2110 (3)
				820 (2)
				930 (3)
SiH_4 [16]	SiH	1·54	8·9	2190
	HH	2·31		2180 (3)
				980 (2)
				910 (3)
CCl_4	CCl	1·755 [17]	—	460
	ClCl	2·87		760 (3)
				220 (2)
				310 (3)

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[8] Cf. this section in last year's Reports.

[9] N. Ginsburg and E. F. Barker, *J. Chem. Physics*, 1935, **3**, 668.

[10] *Physical Rev.*, 1935, **48**, 868.

[11] W. H. J. Childs, *Proc. Roy. Soc.*, 1936, *A*, **153**, 555.

[12] A. H. Nielsen and H. H. Nielsen, *Physical Rev.*, in the press.

[13] D. M. Dennison and M. J. Johnston, *ibid.*, 1935, **47**, 93.

[14] G. E. MacWood and H. C. Urey, *J. Chem. Physics*, 1936, **4**, 402.

[15] A. H. Nielsen and H. H. Nielsen, *Physical Rev.*, 1935, **48**, 861.

[16] W. B. Steward and H. H. Nielsen, *ibid.*, 1935, **47**, 828; F. B. Stitt and D. M. Yost, *J. Chem. Physics*, 1936, **4**, 82.

[17] Electron-diffraction values. Cf. L. O. Brockway, *Rev. Mod. Physics*, 1936, **8**, 231.

[18] J. E. Rosenthal, *Physical Rev.*, 1934, **46**, 730.

have been given for the moment of inertia of methane. The first one[9] is that deduced from the investigation of the deuteromethane molecule and is presumably the most accurate value. The other values have been deduced from the CH_4 bands only, by the method of M. Johnston and D. M. Dennison,[10] and are the ones which should be compared with that given for CD_4, the latter having been obtained by a similar method from observations solely on CD_4.

In addition to those in Table III, the following molecules and ions are known to belong to this class and have had their vibration frequencies determined with a reasonable degree of certainty : PH_3,[20, 21] PD_3,[22] AsH_3,[20] PF_3,[1] PCl_3,[1] PBr_3,[23] AsF_3,[1] $AsCl_3$,[1] $SbCl_3$,[1] $BiCl_3$,[23]

TABLE III.

Symmetrical-top Molecules.

NH_3	NH 1·016 [19]	I_A 2·782 [19]	3330 [20]
	HH 1·645		(3450)(2)
	h 0·36	I_C 4·497	1630 (2)
			950
ND_3	ND 1·016 [19]	I_A 5·397 [19]	2420 [20]
	DD 1·645		(2560)(2)
	h 0·36	I_C 8·985	1160 (2)
			750
CH_3D [9]	CH 1·093	I_A 7·166	2980
	CD 1·093		2210
	HH 1·785	I_C 5·298	1310
			3030 (2)
			1480 (2)
			1160 (2)
CD_3H [13]	CH 1·09	—	(2100)
	CD 1·09		(2990)
	DD 1·8		(990)
			(2220)(2)
			(1290)(2)
			(1020)(2)
CH_3F [10]	CF 1·6	I_A 39·5	2970
	CH 1·1		1480
	HH 1·8	I_C 5·61	1050
			2990 (2)
			1480 (2)
			1200 (2)
CH_3Cl [10]	CCl 1·6	I_A 50·0	2970
	CH 1·1		1350
	HH 1·8	I_C 5·4	732
			3050 (2)
			1460 (2)
			1020 (2)

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[19] M. V. Migeotte and E. F. Barker, *Physical Rev.*, 1936, **50**, 418.

[20] J. B. Howard, *J. Chem. Physics*, 1935, **3**, 207.

[21] L. W. Fung and E. F. Barker, *Physical Rev.*, 1934, **45**, 238.

[22] M. de Hemptinne and J. M. Delfosse, *Bull. Acad. roy. Belg.*, 1935, **21**, 793; G. B. B. M. Sutherland and G. K. T. Conn, *Nature*, 1936, **138**, 641.

[23] J. B. Howard and E. B. Wilson, *J. Chem. Physics*, 1934, **2**, 630.

BF_3,[25] BCl_3,[24, 25] BBr_3,[25] NO_3',[26] CO_3'',[26] CH_3Br,[1] CH_3I,[1] $CHCl_3$,[1] $CHBr_3$,[1] $POCl_3$,[1] and C_2H_6.[27] A certain amount of knowledge is available about their dimensions both from spectroscopic and from diffraction sources, but it is not sufficiently complete to warrant its inclusion here without more discussion than space permits.

Besides those in Table IV, the following molecules may be said to have had their fundamental frequencies assigned beyond reasonable doubt : sulphur dioxide,[7] nitrogen dioxide,[7] and chlorine dioxide.[1]

TABLE IV.

Asymmetrical-top Molecules.

H_2O	OH 0·955	I_A 1·009	3650 [28]
	α 105°	I_B 1·901	3760
		I_C 2·908	1600
D_2O	OD 0·955	—	2670 [29]
	α 105°	—	2780
			1180
HOD	As above	—	2720 [29]
			3720
			1400
H_2S	SH 1·35	I_A 2·68	2615
	α 92°	I_B 3·08	2650
		I_C 5·85	1265
D_2S	As above	—	1900 [30]
		—	1940
			900
HSD	As above	—	1910 [30]
			2620
			1080
CH_2O	CH 1·04	I_A 24·3	2970
	CO 1·2	I_B 21·4	2800
	HH 1·88	I_C 2·9	1740
			1460
			1040
			920
CH_2D_2 [9, 13]	CH 1·09	—	(2140)(1420)
	CD 1·09		(2230) 1240
			(2970) 1040
			(3010) 1090
			(1320)

The references cited should be consulted for the state of current knowledge regarding their exact dimensions. In the following cases there is still a certain doubt about the assignment of one, or at most

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[24] A. B. D. Cassie, *Proc. Roy. Soc.*, 1935, *A*, **148,** 87.

[25] T. F. Anderson, E. N. Lassettre, and D. M. Yost, *J. Chem. Physics*, 1936, **4,** 703.

[26] A. C. Menzies, *Proc. Roy. Soc.*, 1931, *A*, **134,** 265.

[27] E. Bartholomé and H. Sachsse, *Z. physikal. Chem.*, 1935, *B*, **30,** 40.

[28] D. Bender, *Physical Rev.*, 1935, **47,** 252.

[29] E. F. Barker and W. W. Sleator, *J. Chem. Physics*, 1935, **3,** 660; E. Bartholomé and K. Clusius, *Z. Elektrochem.*, 1934, **40,** 530.

[30] C. R. Bailey, J. W. Thompson, and J. B. Hale, *J. Chem. Physics*, 1936, **4,** 625; A. H. Nielsen and H. H. Nielsen, *ibid.*, p. 229.

two, of the fundamentals : ozone,[7] oxygen fluoride,[7] chlorine monoxide,[7, 31] ethylene,[32, 33] nitrosyl chloride,[1] formic acid,[34] oxalic acid,[35] acetic acid.[36] Although enormous numbers of complex molecules have been investigated, the analysis of their vibration spectra has only been partial (certain groups being recognised by their characteristic frequencies), and here we can only refer to a few of the more important contributions to structural problems.

Particular Structural Problems.—The molecule which continues to receive most attention is that of benzene, and the past year is remarkable for the number of important papers concerning it. The most outstanding come from a group of workers [37] in University College who have made a very thorough study of the infra-red, Raman, and fluorescence spectra of benzene and hexadeuterobenzene. The importance of their work lies in the fact that until this was done the coincidences between infra-red and Raman frequencies in the spectrum of benzene made it appear as though the molecule did not possess that hexagonal symmetry which modern resonance theories demand. They have been able to show that these coincidences are either accidental or else are due to a breakdown of the strict selection rules in the liquid state. They have also been able to identify many of the 20 fundamental frequencies. O. Redlich and W. Stricks [38] from observations on the Raman spectra of mono-, di-, and tetra-deuterobenzene have also been able to correlate the frequencies of benzene and to correct earlier provisional assignments by E. B. Wilson.[39] C. Mannebach [48] has made an analysis of the data on the isotopic molecules to evaluate many of the constants of a very general potential function for the force field in benzene. He has shown that appreciable interaction occurs between non-adjacent carbon atoms.

The other important development is the use of infra-red and Raman spectra for the detection of hydrogen bonds, particularly in molecules containing hydroxyl groups. It is manifested either by a shift in the position of the frequency characteristic of the

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[31] R. Pohlmann and H. J. Schumacher, *Z. Physik*, 1936, **102**, 678.

[32] E. Teller and B. Topley, *J.*, 1935, 885.

[33] L. G. Bonner, *J. Amer. Chem. Soc.*, 1936, **58**, 34.

[34] G. Herzberg and H. Verleger, *Physikal. Z.*, 1936, **37**, 444; J. Gupta, *Indian J. Physics*, 1936, **10**, 117, 313; C. S. Venkateswaran, *Proc. Indian Acad. Sci.*, 1935, **2**, *A*, 615; *Current Sci.*, 1936, **4**, 736; P. B. Sarkar and B. C. Ray, *Nature*, 1936, **137**, 495.

[35] J. H. Hibben, *J. Chem. Physics*, 1935, **3**, 675; W. R. Angus and A. H. Leckie, *ibid.*, 1936, **4**, 83, 324.

[36] W. R. Angus, A. H. Leckie, and C. L. Wilson, *Nature*, 1935, **135**, 913.

[37] W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, *J.*, 1936, 912—971.

[38] *Monatsh.*, 1936, **68**, 374; *J. Chem. Physics*, 1935, **3**, 834.

[39] *Physical Rev.*, 1934, **46**, 146.

OH vibration or by its non-appearance. The particular applications of this[40] would take too much space to be summarised adequately here, particularly as many of them are still rather controversial subjects.

Intramolecular Forces.

Next in importance to the dimensional constants of a molecule come those characterising the forces required to alter the distances between the constituent atoms, since they presumably bear a fairly direct relation to the strengths of the corresponding chemical bonds. The magnitudes of the vibration frequencies of a molecule depend solely on the masses of the various atoms and on the forces brought into play when the latter are displaced from their equilibrium positions. A proper analysis of the vibration spectra of a molecule should therefore give information concerning this interatomic force field. The early steps in this direction have already been reviewed in these Reports,[41] but much progress has been made in the past two years. We shall accordingly treat this problem from a more general standpoint and endeavour to show how the various methods are related to one another.

It is well known that in a system executing simple harmonic motion the potential energy may be expressed as $\frac{1}{2}kx^2$, where x is the co-ordinate which varies harmonically, and kx is the restoring force called into play when the system is displaced from its equilibrium position in which x is zero. For example, in a diatomic molecule, x describes the variation in the internuclear distance during the vibration, the frequency of which is given by $2\pi\sqrt{k(m_1 + m_2)/m_1m_2}$, m_1 and m_2 being the masses of the atoms. The force constant k may therefore be directly determined from the vibration frequency. In the case of a polyatomic molecule consisting of n atoms, the matter is not so simple. The $3n - 6$ internal degrees of freedom may each be characterised by a co-ordinate x_r; the corresponding general expression for the potential energy is

$$V = \tfrac{1}{2}\{k_1x_1{}^2 + k_2x_2{}^2 + \ . \ . \ . + 2k_{12}x_1x_2 + 2k_{23}x_2x_3 \ . \ . \ . \} \quad . \quad (1)$$

Using the methods of classical mechanics, one obtains expressions for the $3n - 6$ frequencies of the form $\nu = f(k_1 \ . \ . \ . \ k_{12} \ . \ . \ . \ m_1 \ . \ . \ .)$. In other words there are only $3n - 6$ equations from which to determine all the force constants k_1, k_2, . . . k_{12} . . . etc. Clearly this is impossible, unless some assumption is made which reduces the

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[40] L. Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2680; 1936, **58**, 94; L. Onsager, *ibid.*, p. 1486; R. H. Gillette and A. Sherman, *ibid.*, p. 1135; R. H. Gillette and F. Daniels, *ibid.*, p. 1139; W. Gordy, *J. Chem. Physics*, 1936, **4**, 750.

[41] *Ann. Reports*, 1934, **31**, 21.

number of arbitary constants in (1) to not more than $3n - 6$. All theories of the intramolecular force field are directed towards surmounting this difficulty by making some specific assumption regarding the nature of the field which will effect the required reduction. It is, of course, desirable that the number of constants to be determined should be less than $3n - 6$, for there must then exist certain relations between the frequencies and the atomic masses which are independent of the force constants. The exactness with which these relations are fulfilled forms a test of the validity of the assumptions. We shall consider briefly the types of assumption which have been tried, and how these are related to the chemical conceptions of the bonds in a molecule.

The Valency Force Field.—The assumption which is based most directly on chemical ideas is that of the valency force field.[42] Here each chemical bond in the molecule has associated with it a force constant, k (analagous to that for a diatomic molecule), while the angles between neighbouring bonds each have a characteristic constant, θ, measuring their resistance to deformation. This means that the vibrations of the molecule are described in terms of the changes in the lengths of the bonds (d), and of the angles between the bonds (α), the potential energy being written

$$V = \tfrac{1}{2}\{k_1d_1^2 + k_2d_2^2 + \ . \ . \ . + \theta_1\alpha_1^2 + \theta_2\alpha_2^2 + \ . \ . \ . \}$$

The number of arbitrary constants is obviously considerably reduced, since all interaction terms of the type $2k_{12}x_1x_2$ have been omitted. The valency force field is therefore essentially an inadequate representation, in that one assumes that the only forces acting on the atoms are those resisting simple stretching and deformation of the bonds, and (what is more important) that these stretchings and deformations are quite independent of one another. Nevertheless, it has been applied not unprofitably to a great number of molecules by many different workers over a number of years, and it is only recently that its limitations and value have been critically examined.

For the symmetrical triatomic molecule XYX, only two constants are required to describe this field, one giving the force needed to alter the length of the YX bond, the other giving that needed to alter the XYX angle. This means that a relation must exist between the three frequencies of the molecule, the masses of the atoms, and the angle α between the YX bonds. W. G. Penney and G. B. B. M. Sutherland [7] have tested this relation for the molecules sulphur dioxide, water, deuterium oxide, sulphur dioxide, nitrogen dioxide,

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[42] R. C. Yates, *Physical Rev.*, 1930, **36**, 555; R. Mecke, *Z. physikal. Chem.*, 1931, *B*, **16**, 409, 421; 1932, **17**, 1.

carbon dioxide, carbon disulphide, and the CH_2 group. They found that for all except carbon dioxide and disulphide the discrepancies were less than 5%. On the other hand, the converse process of employing the valency force field to determine the angle α of the molecule cannot be relied on to give a result with an error of less than 20°. For pyramidal molecules of the type YX_3 again only two constants are needed to correlate the four frequencies, so the adequacy of the representation may also be tested here. This has been done for NH_3, ND_3, PH_3 and AsH_3 by Howard[20] and for PF_3, PCl_3, PBr_3, AsF_3, $AsCl_3$, $SbCl_3$, and $BiCl_3$ by Howard and Wilson.[23] The results indicate that as a first approximation the valency force field is reasonably satisfactory, but that interaction forces (particularly in the latter group of molecules) are by no means negligible. For regular tetrahedral molecules of the form YX_4 Rosenthal[18] has made a very careful investigation of CH_4, CCl_4, $SiCl_4$, $TiCl_4$, $SnCl_4$, CBr_4, $SnBr_4$, SO_4'', ClO_4'', and finds that methane is the only one for which the valency force field is a reasonably good approximation. This field has been widely applied by K. W. F. Kohlrausch[43] to many more complex systems. His results may be regarded as a useful confirmation of the general correctness of the assignment of fundamental frequencies; the actual values given for the force constants should not be regarded as more than a first rough approximation to a description of the molecule.

Central Force Field.—Another simple type of force field which was tried out[44] but which has not been so successful is based on the assumption that the only forces which act are directed solely along the lines joining the atoms. Thus if r_{12}, r_{23} . . . denote the distances between the centres of the atoms then the potential energy is written

$$V = \tfrac{1}{2}\{k_1r_{12}^2 + k_2r_{23}^2 + \ldots\ldots\}$$

Although this is possibly a better approximation than the valency force field for certain tetrahedral molecules such as carbon tetrachloride and for some symmetrical plane ions such as CO_3' and NO_3', yet it cannot be said to be very suitable either from a chemical or from a physical point of view. Attempts to improve it by bringing in additional forces have been made by H. C. Urey and C. A. Bradley[45] and by A. Eucken and F. Sauter.[46]

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[43] *Monatsh.*, 1936, **68**, 349; *Z. physikal. Chem.*, 1935, *B*, **30**, 298. These are only two typical examples from a very large number. They are chosen here because they are referred to in Table V.

[44] N. Bjerrum, *Verhandl. deut. physikal. Ges.*, 1914, **16**, 737; D. M. Dennison, *Phil. Mag.*, 1926, **1**, 195.

[45] *Physical Rev.*, 1931, **38**, 1969.

[46] *Z. physikal. Chem.*, 1934, *B*, **26**, 463.

More General Types of Force Field.—A more general method of approaching the problem has been pursued by J. E. Rosenthal,[47] C. Mannebach,[48] G. B. B. M. Sutherland and D. M. Dennison [49] and others. Assuming that the potential function possesses the same geometric symmetry as does the molecule itself, they investigate the minimum number of arbitrary constants required in the general potential function (1). Thus for the isosceles triangular molecule YX_2 it is 4, for the regular pryamidal YX_3, 6, for the regular tetrahedral YX_4, 5, for axially symmetrical ZYX_3,[50] 9, for ethylene,[51] 15, and for benzene,[48], 34. The corresponding number of fundamental frequencies in such molecules being respectively 3, 4, 4, 6, 12, and 20, some further reduction is still necessary. This has been attempted in two ways, either by introducing some generalised type of valency force field which does take account of the more important interactions,[23, 25, 33, 48, 51] or alternatively, by assuming that certain groups in the molecule are practically independent of the rest of the molecule. The latter assumption is sufficiently justified by a mass of empirical data showing that whenever certain groups are present in a molecule certain characteristic frequencies appear in its vibration spectra. It was first applied to the CH_2 and the CH_3 groups in some simple compounds by Sutherland and Dennison;[49] its generalised extension to the series of molecules methane, methyl chloride, chloroform, and carbon tetrachloride by H. H. Voge and J. E. Rosenthal [52] has proved it to be a reliable method of computing the frequencies of a molecule from a knowledge of the force constants of its constituent groups. It should be emphasised that the values of the potential constants in this method may not always be capable of a direct physical interpretation; yet certain combinations of them can be shown to be equivalent to the " bond strengths " (k_1, k_2 . . .) of the valency force field.

There are, however, two methods (each applicable to a limited class of molecule) whereby all the constants of the Rosenthal–Mannebach generalised function may be found. The first is from the isotope effect; if the molecule concerned contains one or more hydrogen atoms, then when these are replaced by deuterium the frequencies are altered while the potential constants remain the same. One has consequently two or more sets of frequencies from which to determine the same set of constants. This has been done for

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[47] *Physical Rev.*, 1934, **45**, 538; **46**, 730; 1935, **47**, 235; 1936, **49**, 535.

[48] *Ann. Soc. sci. Bruxelles*, 1935, *B*, **55**, 5, 129, 237; Van den Bossche and C. Mannebach, *ibid.*, 1934, **54**, 230.

[49] *Proc. Roy. Soc.*, 1935, *A*, **148**, 250.

[50] J. E. Rosenthal and H. H. Voge, *J. Chem. Physics*, 1936, **4**, 134.

[51] J. M. Delfosse, *Ann. Soc. sci. Bruxelles*, 1935, **55**, 114.

[52] *J. Chem. Physics*, 1936, **4**, 137.

ammonia [19] and methane [9] and will doubtless soon be extended. The other method depends on the interpretation of the anomalous spacing of the rotation lines in the degenerate vibrations of symmetrical-top and spherical molecules. This has been accomplished by Johnston and Dennison,[10] who have extended the earlier work of E. Teller [53] on this subject, *viz.*, the interaction between vibration and rotation, and have applied it to the calculation of the five potential constants of methane.

In all of the above methods no account has been taken of possible cubic terms in the potential function, *i.e.*, of the anharmonicity of the vibrations. The frequencies employed in the calculations should therefore not be the observed ones but the frequencies for infinitesimally small amplitude of vibration. The latter can be deduced from the observational data provided a number of the overtone frequencies are known. The errors introduced from this cause are probably not more than a few units %. Another common feature of all of the methods is that certain constants or combinations of them (in particular, the bond constants of the valency force field) differ very little no matter which approach is employed; it is the interaction constants which differ very greatly on the various theories. Fortunately, the bond constant, *i.e.*, the force required to stretch a definite bond a given distance, is of more chemical interest than the latter at the moment. Accordingly we have gathered together in Table V a number of the values now available for some of the commoner bonds. In this connection it is important to note the work of R. M. Badger [54] and C. H. D. Clark [55] on the relation between the force constant and the internuclear distance in a bond. Originally given for diatomic molecules as an extension of Morse's relation $r^3\omega = \text{const.}$, it has since been modified by several workers [56] in attempts to correlate it with the position of the two atoms in the periodic table and to make it applicable to polyatomic molecules. The most convenient form in which to state it is possibly that used by Badger himself, *viz.*,

$$r_e = (C_{ij}/k_e)^{\frac{1}{3}} + d_{ij}$$

where r_e is the equilibrium internuclear distance, k_e is the bond force constant, C_{ij} and d_{ij} are constants the values of which depend on the positions of the constituent atoms in the periodic table. If a force constant for a particular bond is evaluated by the methods we have

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[53] "Hand- und Jahrbuch der Chemischen Physik," 1934, Band 9/11.

[54] *J. Chem. Physics*, 1934, **2**, 128.

[55] *Phil. Mag.*, 1934, **18**, 459.

[56] R. M. Badger, *J. Chem. Physics*, 1935, **3**, 710; C. H. D. Clark, *Phil. Mag.*, 1935, **19**, 476; *Physical Rev.*, 1935, **47**, 238; *Trans. Faraday Soc.*, 1935, **31**, 1017; *Proc. Leeds Phil. Soc.*, 1936, **3**, 218, 221; H. S. Allen and A. K. Longair, *Phil. Mag.*, 1935, **19**, 1032; W. Lotmar, *Z. Physik*, 1935, **93**, 528; M. L. Huggins, *J. Chem. Physics*, 1935, **3**, 473; 1936, **4**, 309.

been considering, this relation enables the corresponding internuclear distance to be computed. This has been done for several molecules,[23, 25, 33, 48, 51] and the results are in surprisingly good agreement with the distances deduced from *X*-ray and electron-diffraction data.

Regarding the values listed in Table V, it is interesting to notice that those below 7 × 10^5 dynes/cm. are associated with single bonds, those between 7 and 15 × 10^5 dynes/cm. with double bonds (in the conventional sense), and those over 15 × 10^5 dynes/cm. with triple bonds. This is important when one remembers that the agreement between various methods is within 10% on any particular molecule. One therefore finds pleasing confirmation that the C–O bond in carbon monoxide and dioxide is nearer triple than single in accordance with the theory of resonance (see p. 45). Similarly the C–C bond in benzene is half-way between a single and a double bond. These examples might be multiplied, but sufficient has been said to indicate the great possibilities of this method of putting a quantitative estimate to the shades of difference between the many types of binding which we are realising exist in chemistry.

G. B. B. M. S.

TABLE V.

Force Constants Characteristic of Bonds in Polyatomic Molecules.

Type of bond.	Force constant, dynes/ cm. × 10^{-5}.	Molecule or group.	Ref.	Type of bond.	Force constant, dynes/ cm. × 10^{-5}.	Molecule or group.	Ref.
C≡C	15·7	C_2H_2	49	N—H	6·4	NH_3	20
C≡N	17·9	HCN	7	S—H	4·0	H_2S	7
	16·7	ClCN	7	C—H	5·9	C_2H_2	49
	16·9	BrCN	7		5·8	HCN	7
	16·7	ICN	7		5·0	CH_4	49
	17·5	C_2N_2	6		4·9	,,	52
N≡N	14·6	NNO	7		5·0	C_2H_4	33
	15·0	N^-	7		4·8	CH_2	7
	22·0	N_2	—		5·0	C_6H_6	43
C=C	9·5	C_2	49	C—C	5·0	C_2H_6	49
	9·8	C_2H_4	49		4·8	C_2N_2	6
	8·6	,,	51		7·6	C_6H_6	43
	8·2	,,	53	C—O	4·5	C_2H_6O	43
C=O	13·4	OCH_2	49	C—S	3·0	C_2H_6S	43
	14·2	OCS	7	C—F	5·8	CH_3F	49
	15·3	OCO	7	C—Cl	3·6	CH_3Cl	49
	19·0	CO	49		3·4	,,	52
N=O	9·1	NO_2	7		5·2	ClCN	7
	13·7	NNO	7	C—Br	2·9	CH_3Br	49
S=O	10·0	SO_2	7		4·2	BrCN	7
C=S	7·6	CS_2	7	C—I	2·3	CH_3I	49
	8·0	OCS	7		3·0	ICN	7
O—H	7·0	H_2O	57				

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[57] J. H. Van Vleck and P. C. Cross, *J. Chem. Physics*, **1933, 1, 357.**

4. ELECTRON DIFFRACTION AND THE STRUCTURES OF GASEOUS MOLECULES.

Theoretical.—In 1915 P. Debye [1] and P. Ehrenfest [2] independently developed equations giving the angular distribution of the intensity of X-rays when scattered by non-crystalline substances; these are particularly applicable to scattering by a gas or vapour, since the molecules are sufficiently far apart to make intermolecular effects negligible in comparison with the total scattered radiation. The observed effects then virtually result only from scattering by atoms within the individual molecule, and the random movements of the latter do not affect the interference of X-rays. Electron waves, the existence of which can now be regarded as definitely established, behave like X-rays in so far as they are scattered by individual atoms in a given molecule, and H. Mark and R. Wierl [3] found that the intensity of the coherent (elastic) scattering for high-velocity electrons could be represented by an equation similar to that of Debye and Ehrenfest; thus, at an angle θ between the primary and the scattered electron beam, the intensity $I_{co.}$ of the latter is given by

$$I_{co.} = k\sum_i\sum_j \psi_i\psi_j \frac{\sin x_{ij}}{x_{ij}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant, ψ is the scattering factor of the particular atom for electrons, and

$$x_{ij} = (4\pi/\lambda) \, . \, l_{ij} \sin \theta/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the term l_{ij} being the distance between the atoms designated by i and j. The equivalent wave-length of the electrons, λ, is determined by the relationship

$$\lambda = \sqrt{\frac{150}{V}} \cdot \frac{1}{1 + 4{\cdot}91 \times 10^{-7}V} \times 10^{-8}\,\text{cm.} \quad . \quad . \quad . \quad (3)$$

where V is the potential in volts applied to accelerate the electrons. In this equation, the first term is the equivalent of the de Broglie equation, $\lambda = h/mv$, and the second term is the relativity correction.

In determining the total coherent scattering by means of equation (1), it is necessary to sum the terms for all possible pairs of atoms in the molecule; the scattering due to individual atoms must be included, and this is given for each atom by the corresponding ψ^2, since now $i = j$ and consequently x_{ij} is zero and $(\sin x_{ij})/x_{ij}$ is unity.

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[1] *Ann. Physik*, 1915, **46**, 809.

[2] *Vers. K. Akad. Amsterdam*, 1915, **32**, 1132.

[3] *Naturwiss.*, 1930, **18**, 205, 778; *Z. Physik*, 1930, **60**, 741; *Z. Elektrochem.*, 1930, **36**, 675; R. Wierl, *Physikal. Z.*, 1930, **31**, 366, 1028.

If free rotation is possible within the molecule, then the distance l_{ij} between a given pair of atoms may not remain constant, and allowance for this variation must be made in the calculations.[4]

Strictly speaking, the factor ψ varies with the scattering angle θ, and for the ith atom is given by the formula

$$\psi_i = \frac{Z_i - F_i}{[(\sin\theta/2)/\lambda]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Z_i being the atomic number of the atom and F_i its scattering, or "form," factor for X-rays.[5] The form factors, which decrease as $(\sin\theta/2)/\lambda$ increases, have been calculated by R. W. James and G. W. Brindley,[6] and by L. Pauling and J. Sherman,[7] the values of the latter authors being, apparently, in better agreement with experiment.[8]

In addition to the coherent scattering already considered, allowance must be made for incoherent scattering, consisting of electrons which have undergone change of wave-length. According to L. Bewilogua,[9] this is given by the relation

$$I_{\text{inco.}} = k\sum_i Z_i f(v_i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which $f(v_i)$ is a function of v_i, and

$$v_i = 4\pi(0{\cdot}176/Z_i^{2/3})(\sin\theta/2)/\lambda \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The values of $f(v_i)$ for various values of v_i are quoted by Bewilogua. It appears from his calculations that for electron diffraction the intensity of the incoherent scattering, which is added to the coherent amount so as to give the total scattering, falls off rapidly as $(\sin\theta/2)/\lambda$ increases and becomes quite small at appreciable scattering angles, especially if the atomic number is large.

The coherent scattering may be divided into two parts: first, "atomic" scattering due to individual atoms, and secondly, "molecular" scattering in which two atoms are concerned. The former, as shown above, is given by ψ^2 for each atom and hence falls off continuously as the scattering angle increases, but the expression for the latter contains the $(\sin x)/x$ terms of equation (1),

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[4] R. Wierl, *Physikal Z.*, 1930, **31**, 266; *Ann. Physik*, 1932, **13**, 453; L. E. Sutton and L. O. Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473; see also, S. H. Bauer, *J. Chem. Physics*, 1936, **4**, 406.

[5] H. Bethe, *Ann. Physik*, 1928, **87**, 55; 1930, **5**, 325; N. F. Mott, *Proc. Roy. Soc.*, 1930, *A*, **127**, 658.

[6] *Phil. Mag.*, 1931, **12**, 81, 729 (correction).

[7] *Z. Krist.*, 1932, **81**, 1.

[8] See R. W. G. Wyckoff, *ibid.*, 1930, **75**, 532; cf. V. E. Cosslett, *Trans. Faraday Soc.*, 1934, **30**, 987.

[9] *Physikal. Z.*, 1931, **32**, 740; 1932, **33**, 688.

and hence passes through a series of maxima and minima as θ increases. If a beam of high-velocity electrons after traversing a gas in an appropriate manner falls on a photographic plate, and this is examined photometrically after development, the record shows a steadily decreasing background intensity, due mainly to atomic, and at small scattering angles also to incoherent, scattering, with occasional inflexions corresponding to the maxima in the coherent scattering. Visual examination of the plate appears to show, however, a central spot, caused by the unscattered electron beam, surrounded by a series of concentric diffraction rings, apparently alternately light and dark, suggesting a series of maxima and minima of scattering without a falling background. This is nevertheless a purely psychological effect, since photometric investigation gives an intensity curve of the type anticipated from theoretical considerations, the positions of apparent maximum density in the diffraction rings corresponding approximately to the inflexions in the curve.

Experimental Methods and Interpretation of Results.—The experimental method in general use is based on that devised by R. Wierl,[10] although important modifications have been made.[11] A fine beam of electrons, accelerated by a potential of about 50,000 volts, is made to pass at right angles through a narrow stream of the gas or vapour under investigation, and then falls on a photographic plate. The electrons are produced either by a heated cathode in a high-vacuum type of discharge tube, or by gas-discharge, in either air or hydrogen, using a cold cathode. Although some authors have used the latter, at the California Institute of Technology, where the most important recent work on electron-diffraction of vapours has been done, the hot cathode is preferred.[12] The electron-accelerating voltage is measured either by an electrostatic (or other) voltmeter, or else by a milliammeter in series with a suitable resistance; the instrument is calibrated with the aid of electron-diffraction photographs obtained through thin gold foil, for which the space-lattice dimensions are accurately known,[13] or by the use of ammonium chloride.[14] A method for studying electron diffraction by gases in which a relatively low voltage, *viz.*, 6,400 volts, is employed has been described recently [15]; it is not capable, however, of giving such accurate results as the high-voltage method.

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[10] *Ann. Physik*, 1931, **8**, 521.

[11] V. E. Cosslett, *loc. cit.*, ref. (8), p. 981; H. de Laszlo, *Proc. Roy. Soc.*, 1934, *A*, **146**, 672; L. O. Brockway, *Rev. Mod. Physics*, 1936, **8**, 231.

[12] L. O. Brockway, *loc. cit.*, p. 240.

[13] E. A. Owen and J. Iball, *Phil. Mag.*, 1932, **13**, 1020; M. C. Neuberger, *Z. Krist.*, 1936, **93**, 1.

[14] H. Boersch, *Monatsh.*, 1935, **65**, 311.

[15] P. G. Ackermann and J. E. Mayer, *J. Chem. Physics*, 1936, **4**, 377.

Since the quantity x_{ij} in equation (2) depends on the corresponding interatomic distance l_{ij}, it is evident that the positions of the diffraction rings, or the discontinuities in the photometric curve, will be related to the various atomic separations within the molecule, and it was shown by Mark and Wierl[3] that the electron-diffraction patterns could be used to determine interatomic distances in a molecule. The principle of the method is analogous to that previously used in connexion with the scattering of X-rays by gases: certain definite configurations are assumed for the atoms within the given molecule, and the theoretical scattering curves are calculated and compared with the experimental results. The configuration for which the best agreement is obtained is regarded as being correct, and from this the interatomic distances are determined. When the molecule is relatively complex, the calculations may become laborious, although certain simplifications (see below) can be made without involving serious error.

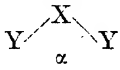
From equation (4) it may be seen that it is possible to write $\psi = Z\phi$, where

$$\phi = (1 - F/Z)/[(\sin \theta/2)/\lambda]^2 \quad . \quad . \quad . \quad . \quad (7)$$

and consequently, as a first approximation, since F, which is always less than Z, decreases as the scattering angle increases (p. 66), equation (1) can be put in the form

$$I_{\text{co.}} \approx k' \sum_i \sum_j Z_i Z_j (\sin x_{ij})/x_{ij} \quad . \quad . \quad . \quad . \quad (8)$$

For a simple molecule, *e.g.*, carbon tetrachloride, the configuration of which can be taken with confidence as tetrahedral, this approximate equation for the coherent scattering can readily be written in terms of one parameter, *e.g.*, $x_{\text{C—Cl}}$, and of the atomic numbers of carbon and chlorine. By taking a series of arbitrary numerical values of x, the corresponding values of $I_{\text{co.}}$ can be calculated and the resulting hypothetical scattering curve, showing a series of maxima and minima, plotted. From the electron-diffraction photograph, or from the photometric curve obtained therefrom, the actual positions of the maxima and minima of scattering are determined and expressed in terms of $(\sin \theta/2)/\lambda$, since θ can be calculated from the corresponding displacement of these positions on the plate and the dimensions of the apparatus, and λ from the accelerating voltage (equation 3). A comparison of the x values for the calculated maxima and minima with the observed $(\sin \theta/2)/\lambda$ values gives an approximate relationship between these two quantities which can be used to calculate the atom-form correction ϕ (equation 7) in terms of x. The approximate $I_{\text{co.}}$ values, for various distances x, are now multiplied by the corresponding ϕ at each point to give the correct coherent scattering intensities, which can now be plotted against x; the new values of the latter for the maxima and minima are then compared with the corresponding observed $(\sin\theta/2)/\lambda$ values, and the distance between the atoms, *e.g.*, $l_{\text{C-Cl}}$, calculated by means of equation (2). If the configuration chosen for the molecule is the correct one, all the maxima and minima should give approximately the same value for the interatomic distance; should this not be the case, however, the configuration is probably incorrect and a new one must be sought which gives more satisfactory constancy. The correctness of any configuration can usually be determined by a general comparison of the diffraction rings and the calculated scattering curve for that configuration. A further correction for incoherent scattering should be made before the final comparison of observed and calculated positions of maxima and minima, but as this quantity diminishes steadily and has to be *added* to $I_{\text{co.}}$, the positions of the inflexions in the curve are not appreciably affected. The main objection to the inclusion of $I_{\text{inco.}}$ is that its rapidly falling value tends to suppress the maxima in the scattering intensity curves and makes their identification difficult: this has been overcome to some extent by plotting the total intensity multiplied by $[(\sin\theta/2)/\lambda]^2$ against x, when definite maxima and minima appear in the curves.[16]

When the configuration of a molecule can only be expressed in terms of two parameters, *e.g.*, for compounds of the type  then it is convenient to chose these as the distance $l_{\text{X-Y}}$ and the valency angle α. The values of $I_{\text{co.}}$ are then plotted against x for different probable values of α, and the general shape of the curve is compared either with the actual diffraction pattern or with its photometer record; the value of α giving a calculated curve showing the best agreement, as far as the positions and intensities of maxima and minima are concerned, is assumed to be the correct one, and from the corresponding curve the distance $l_{\text{X-Y}}$ is calculated. Frequently it is not possible to be quite certain as to which curve gives the best agreement, and then the molecular configuration is in doubt;[17] this weakness of the method will certainly be overcome in time, as the experimental technique is improved.

When more than two parameters are required to define the dimensions and configuration of a molecule, *e.g.*, in benzene derivatives, a large number of calculated intensity curves may have

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[16] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Physics*, 1935, **3**, 699.

[17] See, *e.g.*, L. R. Maxwell, V. M. Mosley, and L. S. Deming, *ibid.*, 1934, **2**, 331.

to be plotted. If something is known about the molecule, as is generally the case, then the calculations are limited to the most probable configurations in the first place. A number of approximations can also be made which do not seriously affect the accuracy of the final results but greatly simplify the calculations; some of these simplifications are mentioned below.[18]

One of the main sources of error in the application of the electron-diffraction method to the determination of interatomic distances lies in the identification of the points on the photometric record corresponding to the maxima and minima of coherent scattering intensity. Since the continuously falling background tends to flatten out the photometric maxima and makes their accurate identification difficult, it is desirable to compensate for the background intensity of the photographic plate. One means of achieving this end is to print the original plate by allowing the incident light to pass through a special revolving sector so designed as to compensate for the steep falling off, from the centre outwards, in background blackening of the plate :[19] this method has the disadvantage that the relative intensities of the various maxima and minima are altered, whereas a knowledge of such intensities is often of importance in determining the correct molecular configuration. An alternative method [20] is to make a special compensating cell having the same shape as the photometric background-scattering curve. This cell is filled with a dark coloured liquid and light is allowed to pass through it and to fall on a photographic plate : the plate will, therefore, become fogged and the density of fogging will be almost the exact reverse of the background blackening of the original plate. The latter and the compensating plate are then placed together and printed on to a third plate, giving a series of sharp dark and light bands; a photometer record of this shows clear maxima and minima of coherent scattering. The compensation process described is particularly valuable for giving accurate measurements of the positions of the first few maxima, but its use is limited to this region; at greater scattering angles the fall in the background and the prominence of the maxima above it become so small that it is almost impossible to construct a compensation cell that will permit of the separation of one from another with any accuracy. It is a remarkable fact, however, that the eye is more sensitive than any mechanical photometer, and it is possible by direct visual examin-

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[18] For full discussion, see L. Pauling and L. O. Brockway, *J. Chem. Physics*, 1934, **2**, 867.

[19] F. Trendelenburg, *Naturwiss.*, 1933, **21**, 173; F. Trendelenburg and E. Franz, *Wiss. Veröff. Siemens-Konz.*, 1934, **13**, 48.

[20] V. E. Cosslett, *loc. cit.*, ref. (11).

ation of the plates to detect ten or more diffraction maxima, as well as several minima. Owing to the intense blackening of the central spot, caused by unscattered electrons, however, the positions of the maxima in the first one or two diffraction rings cannot generally be estimated correctly : this is mainly due to the St. John effect,[21] a physiological phenomenon which militates against the accurate estimate of the position of maximum density of a photographic plate when the rate of decline of the background intensity is different on both sides of the maximum. The effect is also operative when two diffraction rings are close together; under these conditions the photometer and the calculated intensity curves have a "shelf."[22] Measurements liable to be in error because of the St. John effect should not be used in the final calculations, although the approximate positions of the diffraction maxima may be used for purposes of qualitative comparison with the positions in the calculated intensity curves, in order to determine which of these represents the correct molecular configuration.

Approximation Methods.—In applying the correction for the atom-form factor (equation 7), it is found that the value of ϕ approaches a constant as the scattering angle increases, so that for the higher orders of maxima and minima ψ may be replaced by Z, the atomic number, without appreciable error; consequently, under conditions such that visual identification of the positions of maxima and minima is satisfactory, the approximate equation (8) can be used with reasonable accuracy. This simplification was introduced by Wierl,[4] and it has been subsequently confirmed that the use of Z instead of ψ does not introduce any appreciable error in the calculation of interatomic distances. Although some authors use the simple form of the scattering-intensity equation in conjunction with the photometric method of identifying the positions of inflexions, it has been shown by L. Pauling and L. O. Brockway,[18] in a very comprehensive study of the visual method of observing the maxima and minima in diffraction photographs, that there is reason for supposing that because of the nature of the background the eye automatically corrects, at least approximately, for the difference between Z and ψ. Quite accurate results should, therefore, be obtained by supposing the scattering factor of an atom to be proportional to its atomic number, and finding the positions of apparent maxima and minima of scattering, other than the first one or two, by visual examination: under these conditions incoherent scattering can be neglected in calculating the intensity values. The conclusion is borne out by the fact that, using this

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[21] E. C. St. John and L. W. Ware, *Astrophys. J.*, 1916, **44**, 35.

[22] L. O. Brockway and F. T. Wall, *J. Amer. Chem. Soc.*, 1934, **56**, 2373.

method, Pauling and Brockway found the C–Cl distance in carbon tetrachloride to be 1·76 A., whereas the careful work of V. E. Cosslett,[11, 23] who applied corrections for the atom-form factor and for incoherent scattering, and also compensated for background scattering in determining the positions of the first few maxima and minima, led to a value of 1·74 ± 0·02 A. The accuracy of interatomic distances obtained by electron-diffraction methods is generally stated to be ± 1%.

A further approximation made by some workers, in order to simplify the calculations for molecules containing both light and heavy atoms, is to ignore the scattering due to the lightest atoms, *e.g.*, hydrogen; this is justified by the fact that the scattering factor of an atom is approximately proportional to its atomic number. In halogenobenzenes, for example, the intensity of the scattering caused by halogen–carbon and by halogen–halogen is so large compared with that due to carbon–carbon, hydrogen–carbon, or hydrogen–hydrogen, that the corresponding scattering terms of these latter in the intensity equation (8) may be neglected without serious error. Using this simplified procedure and the visual method of examining the diffraction photographs, H. de Laszlo [24] obtained 2·05 ± 0·01 A. for the C–I distance in *p*-di-iodobenzene, based on the positions of twelve scattering maxima, whereas S. B. Hendricks and his co-workers,[25] who studied the photometric records of the plates, applied corrections for atom-form factors, and took into consideration the scattering from all the atoms, gave 2·00 A. (probably, at least, ± 0·05). It may be concluded, therefore, that until there is a marked improvement in the technique, which permits of more accurate identification than is at present possible of the positions of maxima and minima in the electron-diffraction photographs, the application of the approximations described can be generally justified.[26]

Analytic Method.—An analytical procedure which facilitates the accurate interpretation of electron-diffraction photographs has been proposed by S. H. Bauer [27] : the first step involves the differentiation of equation (8) so that the positions of maxima and minima of scattering are given by

$$\sum_i \sum_j Z_i Z_j \left(\cos x_{ij} - \frac{\sin x_{ij}}{x_{ij}} \right) = 0 \quad . \quad . \quad . \quad (9)$$

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[23] See also V. E. Cosslett and H. de Laszlo, *Nature*, 1934, **134**, 63.

[24] *Proc. Roy. Soc.*, 1934, *A*, **146**, 690.

[25] S. B. Hendricks, L. R. Maxwell, V. L. Mosley, and M. E. Jefferson, *J. Chem. Physics*, 1933, **1**, 549.

[26] See, however, L. R. Maxwell *et al.*, *loc. cit.* ref. (16).

[27] *Loc. cit.*, ref. (4).

As before, a probable configuration is chosen with definite values of l_{ij}; these are inserted in equation (9) together with a value of $(4\pi/\lambda)\sin\theta/2$ representing the position of an observed maximum or minimum, and if the parameters chosen are correct, the sum of the terms will reduce to zero for every maximum and minimum. As it is improbable that the first model tried will be the right one, the equations will, in general, lead to a set of residuals, and Bauer has shown how by a process of successive approximation it is possible to obtain a set of l_{ij} values which satisfy equation (9). These only represent the true inter-atomic distances, however, if the values chosen arbitrarily at the commencement of the calculation are close to the correct ones. Only the positions of sharp, well-defined rings may be used in the calculation, and maxima associated with a "shelf" or a low "trough" should be ignored. Although the method may be useful in certain cases, the limitations are such as to prevent it from being generally applicable until improvements in technique permit more complete diffraction patterns to be obtained.

Radial Distribution Method.—L. Pauling and L. O. Brockway[28] have described a procedure, known as the "radial distribution method," for the examination of electron-diffraction rings which is related to that used for the interpretation of *X*-ray diffraction patterns obtained with liquids.[29] It has the advantage of not requiring any assumption or previous knowledge concerning the configuration of the molecule or of inter-atomic distances. A distribution function for scattering power is calculated representing, in terms of l, the product of the scattering powers in volume elements, instead of by atoms, at a distance l apart. Since the electrons are scattered mainly by atomic nuclei, a maximum in the function represents an inter-nuclear distance in the molecule equal to the corresponding value of l; thus the inter-atomic distance is determined. The theoretical intensity equation (1) is based on the assumption that discrete atoms act as scatterers, but if the scattering power is regarded as spread over the molecule as a whole, then integration replaces summation, thus

$$I = k''\int_0^\infty \frac{l^2D(l)}{s^4}\cdot\frac{\sin sl}{sl}\,dl \quad . \quad . \quad . \quad . \quad (10)$$

where s is used for $(4\pi/\lambda)\sin\theta/2$, so that sl is identical with x. In this equation $l^2D(l)$ represents the product of the scattering powers in all volume elements at a distance l apart. Equation (10) being written in the form

$$s^5I = k''\int_0^\infty lD(l)\,.\,\sin sl\,.\,dl \quad . \quad . \quad . \quad . \quad (11)$$

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[28] *J. Amer. Chem. Soc.*, 1935, **57**, 2684.

[29] P. Zernike and J. A. Prins, *Z. Physik*, 1927, **41**, 184.

it can be inverted, thus

$$lD(l) = k''' \int_0^\infty s^5 I \,.\, \sin sl \,.\, ds \quad . \quad . \quad . \quad (12)$$

or

$$D(l) = k''' \int_0^\infty s^6 I \, \frac{\sin sl}{sl} \, ds \quad . \quad . \quad . \quad . \quad (13)$$

For practical purposes the integral may be replaced very approximately by a sum

$$D(l) = \sum_n I_n \frac{\sin s_n l}{s_n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which one term appears for every ring in the diffraction pattern; s_n is the s value for the nth ring and I_n is its intensity. The latter quantity is estimated visually for each diffraction ring, and s is calculated from its position determined by the visual method : it is thus possible to evaluate $D(l)$ for a series of l values, generally at intervals of 0·1 A. between 0 and 4 A. The positions of the maxima in the curve of $D(l)$ against l give the distances apart of important scattering centres in the molecule. The method can only be used, at present, for the complete analysis of simple molecules in which there are few important inter-atomic distances involved, and it fails when two of these distances are close together, so that the two separate maxima are fused into one broad one.

Applications.—Bond distances. The interest of electron-diffraction measurements of gaseous molecules lies mainly in two directions: first, for the determination of interatomic distances with the object of testing the Pauling–Sidgwick rule [30] of the additivity of covalent bond distances and the possibility of throwing light on the type of linkage in a given molecule; and secondly, for the investigation of molecular configuration and the evaluation of valency angles. With simple molecules, for which atomic radii obtained from their band spectra are available, it is found that the electron-diffraction method gives results in good agreement with those expected, as may be seen from the following data for the interatomic distances in chlorine,[18] bromine,[18] iodine,[25] and iodine monochloride.[18]

	Interatomic distances, A.	
Molecule.	Electron diffraction.	Band spectra.
Cl—Cl	2·01	1·99
Br—Br	2·29	2·28
I—I	2·64	2·66
I—Cl	2·30	2·31

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[30] N. V. Sidgwick and E. J. Bowen, *Ann. Reports*, 1931, **28**, 385; N. V. Sidgwick, "The Covalent Link in Chemistry," 1933, p. 64; L. Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; see also W. H. Rodebush, *Trans. Faraday Soc.*, 1934, **30**, 778; C. H. D. Clark, *ibid.*, 1935, **31**, 1017.

The I–Cl distance calculated from the Cl–Cl and the I–I value, on the assumption of additivity, is 2·325 A., which differs from the observed results by no more than the experimental error.

Until recently, the C–Cl distance in aliphatic compounds was [25,31] accepted as 1·81—1·83 A., approximately the same value being found in carbon tetrachloride, αα- and αβ-dichloroethane, *cis*- and *trans*-dichloroethylene, tri- and tetra-chloroethylene, and in carbonyl and acetyl chlorides; later work [18,20,23,32] has indicated that the bond distance is actually somewhat less, *viz.*, 1·76 ± 0·02 A., this value having been obtained in all four chloromethanes.[33] Further investigation of the six chloroethylenes has shown that in these substances the C–Cl distance is less than in the chloromethanes and varies from one compound to another : the following distances are given by L. O. Brockway, J. Y. Beach, and L. Pauling [34] : vinyl chloride, 1·69 A.; αα-dichloro-, 1·69 A.; *cis*-dichloro-, 1·67 A.; *trans*-dichloro-, 1·69 A.; trichloro-, 1·71 A.; and tetrachloroethylene, 1·73 A. These results have been interpreted [35] as implying resonance involving two states of the type $>C{=}\overset{|}{C}{-}Cl$ and $>\overset{-}{C}{-}\overset{|}{C}{=}\overset{+}{Cl}$, so that the C–Cl distance tends to approach that for a double bond; in vinyl chloride the shortening should be greatest, since there is only one chlorine atom to take part, but in tetrachloroethylene the effect of the double bond is divided amongst four chlorine atoms and the bond distance should approach the normal single bond value. It may be noted that H. de Laszlo,[36] in a preliminary communication, has given the C–Cl distance in both *trans*-dichloro- and tetrachloro-ethylene as 1·74 A.; this author has also reported the length of the C–Br bond as 1·93 A. in carbon tetrabromide, 1·91 A. in *trans*-dibromoethylene and in tetrabromoethylene, and 1·84 A. in dibromoacetylene; before this, an almost constant distance of 2·05 ± 0·05 A. had been recorded for the four bromomethanes, *tert.*-butyl bromide, *cis*- and *trans*-dibromoethylenes, tribromoethylene, and carbonyl and acetyl bromides.[10,37] Similarly, the constant value of 2·28 ±

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[31] R. Wierl, *locc. cit.*, refs. (4) and (10); J. Hengstenberg and L. Brú, *Anal. Fis. Quim.*, 1932, **30**, 341; S. B. Hendricks *et al.*, *loc. cit.*, ref. (25); R. W. Dornte, *J. Amer. Chem. Soc.*, 1933, **55**, 4126; *J. Chem. Physics*, 1933, **1**, 566.

[32] H. Braune and S. Knoke, *Z. physikal. Chem.*, 1933, *B*, **21**, 297; C. Degard, J. Piérard, and W. van der Grinten, *Nature*, 1935, **136**, 142; C. Degard, *Compt. rend.*, 1935, **201**, 951; *Bull. Soc. chim. Belg.*, 1936, **45**, 15.

[33] L. E. Sutton and L. O. Brockway, *loc. cit.*, ref. (4).

[34] *J. Amer. Chem. Soc.*, 1935, **57**, 2693.

[35] L. Pauling, L. O. Brockway, and J. Y. Beach, *ibid.*, p. 2705.

[36] *Nature*, 1935, **135**, 474.

[37] R. W. Dornte, *J. Chem. Physics*, 1933, **1**, 630.

0·05 A. for the C–I distance in methyl and ethyl iodides, and for methylene iodide,[37, 38] has now been replaced by 2·12 A. in iodoform, 2·10 A. in *trans*-di-iodo- and tetraiodo-ethylene, and 2·03 A. in di-iodoacetylene. It is clear from these results that further accurate investigation on the halogeno-ethylenes and -acetylenes will have to be undertaken before the suggestion of resonance involving double-bonded halogen can be regarded as proved or disproved : it is important to bear in mind that the tendency to form the double bond might be expected to increase in the series Cl, Br, I, but there is hitherto no evidence that this is the case.

In aromatic compounds the carbon–halogen distances are less than in the halogenomethanes, as the following results (in A.) show :

	$-C_{al.}-X.$[38, 39]	$>C_{ar.}-X.$[24, 25]	Additive.
X = Cl	1·76	1·69	1·76
Br	1·93, 1·91	1·88	1·91
I	2·12	2·05, 2·00	2·10

The observed values for the aliphatic compounds are in good agreement with those calculated on the assumption of additivity of covalent bond distances by using the best data in the literature,[40] but with the aromatic compounds a distinct shortening of the bond distance is evident. Here again resonance between two states, $>C_{ar.}-X$ and $>C_{ar.}=X$, has been suggested[35, 41] to account for the difference; resonance of this type, however, not only appears to be out of harmony with chemical reactivity and other properties of aromatic halogen derivatives,[42] but the results seem to be capable of another interpretation. It may be noted in the first place that the $>C_{ar.}-Cl$ distance recorded is for hexachlorobenzene, in which the double-bond character can be divided amongst six atoms : the actual shortening should thus be very small. Further, the same $>C_{ar.}-Br$ distances have been found in di-, tri-, and hexa-bromobenzenes, whereas a steady increase might have been anticipated. From general considerations, the difference between additive and observed bond distances might be expected to increase through the series Cl, Br, I, but there is no evidence that it does so. It is not impossible that the conjugated resonating system of single and double linkages in the benzene nucleus can bring about a " tightening up " of external bonds, and so produce a small discrepancy from the

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[38] L. Brú, *Anal. Fis. Quim.*, 1933, **31**, 115.

[39] Unpublished, see L. O. Brockway, *loc. cit.*, ref. (11), pp. 260—261.

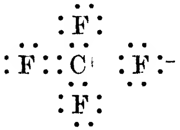
[40] Data from N. V. Sidgwick and E. J. Bowen, *loc. cit.*, ref. (30), pp. 401, 402; N. V. Sidgwick, *op. cit.*, ref. (30), Chap. III; L. Pauling, *loc. cit.*, ref. (30); L. Pauling and M. L. Huggins, *Z. Krist.*, 1934, **87**, 205.

[41] See, *e.g.*, H. P. Klug, *J. Chem. Physics*, 1935, **3**, 747; N. V. Sidgwick, *J.*, 1936, 533 (537).

[42] G. Baddeley, G. M. Bennett, S. Glasstone, and B. Jones, *J.*, 1935, 1827.

additive carbon–halogen distance; there would then be no necessity to postulate resonance and double-bond formation. Some evidence for this view is to be found in the fact that the $C_{al.}$–$C_{ar.}$ distance, obtained from *X*-ray observations on crystals of durene and dibenzyl,[43] are 1·47 A. compared with the value of 1·54 A. for the $C_{al.}$–$C_{al.}$ bond. The electron-diffraction method gives the $C_{al.}$–$C_{ar.}$ distance as 1·50 A. in di-, tri- and hexa-methylbenzenes,[44] which is again less than the normal value. The suggestion might be made that this was due to resonance [45] involving the structures $>C{-}CH_3$ and $>C{=}\overset{-}{C}H_2\overset{+}{H}$, but if this were so, some difference in the C–C distance might be expected according to the number of methyl groups substituted in the nucleus.

The C–F distance in methyl fluoride [46] is 1·42 A., in excellent agreement with the spectroscopic value (1·43 A.) and that based on additivity (1·41 A.), but in carbon tetrafluoride [14, 22] the bond length is 1·36 A., similar values being found in dichlorofluoromethane and dichlorodifluoromethane.[46] It was at one time suggested [22] that the shortening of the bond was due to the partially ionic character of the C–F link resulting from the difference in the electronegativity of the two elements. It should be noted, however, that the ionic distance C^{+}–F^{-} is about 1·53 A., which is actually greater than the corresponding covalent distance; further, the dimensions of the ions are such as to make the structure $C^{4+}(F^{-})_4$ improbable.[47] An alternative view has been proposed by L. Pauling,[48] who considers that, in addition to the single-bonded structure of carbon tetrafluoride, the molecule resonates among structures having an F^{-} ion bound electrostatically to a CF_3^{+} ion in which there is a double bond, as shown in the inset, so that a shortening of the C–F bond distance, determined by the double-bond character which should be shared by all four bonds, would be observed. This resonance would not be possible in methyl fluoride, since only one fluorine atom is present. If this explanation for the length of the C–F bond in tetrafluoromethane is correct, then, it must be pointed out, the shortening of the distance is unexpectedly large. This fact is brought out more clearly by considering the bond dis-



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[43] J. M. Robertson, *Proc. Roy. Soc.*, 1933, *A*, **141**, 594; 1934, *A*, **146**, 473.

[44] P. L. F. Jones, *Trans. Faraday Soc.*, 1935, **31**, 1036.

[45] Compare J. W. Baker and W. S. Nathan, *J.*, 1935, 1844.

[46] Unpublished, see L. O. Brockway, *loc. cit.*, ref. (11), pp. 260, 261.

[47] N. V. Sidgwick, *Ann. Reports*, 1933, **30**, 118; see also M. L. Huggins, *Chem. Reviews*, 1932, **10**, 427.

[48] Quoted by L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036 (2043).

tances in SiF_4,[22] PF_3,[22] and AsF_3,[22] which are as follows, the additive figures being given below each measured value :

	Si–F 1·54	P–F 1·52	As–F 1·72
Additive	1·81	1·74	1·85

The maximum decrease due to the complete formation of double bonds, *i.e.*, 10% of the single bond distances, would be 0·18, 0·17, and 0·18 respectively, whereas the actual differences are 0·27, 0·22, and 0·13. The subject evidently requires further consideration. It has been mentioned in a previous Report [49] that the discrepancies between observed and additive distances in the hexafluorides of sulphur, selenium, and tellurium [50, 51] have been interpreted as implying a tendency towards ionic linkage in all these bonds, but in sulphur hexafluoride, at least, it is not possible to accommodate six fluorine ions (radius 1·33 A.) about the S^{6+} ion (radius 0·3 A.) [52]; even if the latter were extended to 0·55 A., so that the bond distance was equal to the measured value, 1·88 A., this would still not be possible. Resonance of the type postulated above, involving the electrostatically bound structure $SF_5{}^+F^-$, with one fluorine atom doubly bound, might account for the results, but again the effects are very large.

With chlorides there appears to be no tendency for ionisation of the chlorine, since the C–Cl distance in carbon tetrachloride is exactly equal to the additive value;. hence the shortening of the bond in $SiCl_4$ (0·16 A.),[10, 22, 51] $GeCl_4$ (0·13 A.),[10, 53] $SnCl_4$ (0·09 A.),[10, 22] PCl_3 (0·09 A.),[22] and $AsCl_3$ (0·04 A.),[22] must be explained in another manner. It was originally suggested [22] that this might be due to the difference in the electronegativity of the two atoms forming the bond, but this view was disposed of by the fact that in the methyl derivatives of silicon, germanium, tin, nitrogen, and sulphur the distance between each of these atoms and the carbon atom is almost exactly equal to the additive value, in spite of the difference of electronegativity.[54] An alternative explanation is that double-bond formation can occur between the halogen and the central atom, as a result of the latter holding five, or more, pairs of electrons.[22, 54] There is no reason to believe that this increase can occur in the first row of the periodic classification, and for these elements the decrease is not found. In fact a discrepancy in the opposite direction appears to exist between the observed and the

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[49] *Ann. Reports*, 1933, **30**, 93.

[50] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 68.

[51] H. Braune and S. Knoke, *loc. cit.*, ref. (32).

[52] For data, see N. V. Sidgwick, *loc. cit.*, ref. (47); M. L. Huggins, *loc. cit.*, ref. (47).

[53] L. O. Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 958.

[54] L. O. Brockway and H. O. Jenkins, *loc. cit.*, ref. (48).

additive distances for the O–F and the O–Cl bonds in oxygen fluoride and chlorine monoxide,[55] respectively; the values are as follows:

	O–F.	O–Cl.
Observed, A.	1·36 ± 0·10;[55] 1·41 ± 0·05[14]	1·71 ± 0·02[55]; 1·68 ± 0·03[56]
Additive, A.	1·30	1·65

The difference in the case of the fluoride may be due to experimental error, but it is believed not to be so for the O–Cl bond; L. E. Sutton and L. O. Brockway [55] have suggested tentatively that the accepted value for the radius of the singly-linked oxygen atom, 0·66 A., may actually be low by 0·06 A., but it is nevertheless concluded that the rule of additivity of atomic radii is only approximate. It is of interest to note here that the C–O distance in various compounds [55, 57] has been found to be between 1·42 and 1·45 A.,† in good agreement with the additive value 1·43 A.: this result lends support to the accepted oxygen radius. The Cl–O distance in chlorine dioxide [58] is 1·53 A., a value not very different from that to be expected for a double bond between chlorine and oxygen, *viz.*, 1·48 A. The measurements have been used to suggest a structure for chlorine dioxide involving two resonance states, *viz.*, $\colon\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\colon\underset{\cdot\cdot}{\mathrm{Cl}}\overset{\cdots}{\colon}\underset{\cdot\cdot}{\mathrm{O}}\colon$ and $\colon\underset{\cdot\cdot}{\mathrm{O}}\overset{\cdots}{\colon}\underset{\cdot\cdot}{\mathrm{Cl}}\colon\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\colon$; the arguments are based on the probable assumption that the $\mathrm{O}\overset{\cdots}{\colon}\mathrm{Cl}$ distance lies between those for a single and a double bond, since the three-electron linkage is generally equivalent to a single-electron bond.

The distance between singly linked carbon atoms in aliphatic compounds has been found [10, 37, 59] to be 1·50—1·55 A., whereas between adjacent atoms in the benzene nucleus it is 1·39—1·42 A.[10, 18, 24, 25, 44] The C=C double-bond distance in ethylene derivatives is apparently 1·38 A.,[4, 34, 60, 61] in agreement with expectation (see, however, p. 45). The C≡C distance in acetylene [10] and diacetylene [62] is given as 1·20—1·22 A., the latter figure being

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[55] L. E. Sutton and L. O. Brockway, *loc. cit.*, ref. (4).

[56] L. Pauling and L. O. Brockway, *loc. cit.*, ref. (28), recalculated by the radial distribution method.

[57] D. C. Carpenter and L. O. Brockway, *J. Amer. Chem. Soc.*, 1936, **58**, 1270; L. O. Brockway and P. C. Cross, *ibid.*, p. 2406.

[58] L. O. Brockway, *Proc. Nat. Acad. Sci.*, 1933, **19**, 303, 874.

[59] R. Wierl, *Ann. Physik*, 1932, **13**, 453; R. W. Dornte, *loc. cit.*, ref. (31); L. O. Brockway, *loc. cit.*, ref. (46).

[60] L. O. Brockway and P. C. Cross, *loc. cit.*, ref. (57).

[61] R. W. Dornte, *J. Chem. Physics*, 1933, **1**, 566.

[62] L. O. Brockway, *Proc. Nat. Acad. Sci.*, 1933, **19**, 868.

† The observed distance 1·34 ± 0·07 A. proposed for dimethyl and diethyl ethers (L. Brú, *Anal. Fis. Quim.*, 1932, **30**, 486) is probably in error.

identical with the length generally attributed to this linkage; the observed value for the $C\equiv N$ linkage in cyanogen [4, 62] and in acetonitrile,[63] 1·16—1·18 A., is also in excellent agreement with the additive distance 1·16 A. The use of additive values for the carbon–nitrogen and the nitrogen–nitrogen bond in methyl azide [64] gives calculated electron-scattering curves in harmony with the experimental maxima and minima, and the C–N and N–O distances in nitromethane and in α-methylhydroxylamine, respectively, confirm the concept of additivity.[34]

It has been mentioned that the measured length of the singly-linked $C{-}O$ bond is very close to the additive value, but the measurements on the $C{=}O$ bond were at one time confusing, since distances of about 1·13 A. were reported in carbonyl and acetyl chloride and bromide [65] and in formaldehyde,[66] as compared with the expected value of 1·28 A. New measurements on carbonyl chloride,[34] however, give the $C{=}O$ distance as 1·28 A., and a similar result is reported from observations on the dimeric form of formic acid.[66] Distances of the same order, 1·25—1·29 A., have been obtained by the *X*-ray study of crystals of carbonates, oxalic acid, urea, and basic beryllium acetate [67]: it is somewhat surprising, however, to find a distance of 1·14 A. reported for the $C{=}O$ bond in solid benzoquinone.[68] The carbon–oxygen distance in carbon dioxide [10] and in carbon oxysulphide[14, 65, 69] is 1·13 A., according to electron-diffraction measurements, a result in agreement with the value calculated from Raman spectra and from *X*-ray scattering of the former compound. The marked difference between this distance and the additive $C{=}O$ bond value of 1·28 A. has been attributed [70] to resonance between the normal state $O{=}C{=}O$ and the two excited states $^{-}O{-}C\equiv O^{+}$ and $^{+}O\equiv C{-}O^{-}$, for then the carbon–oxygen distance would approach that for the $C\equiv O$ bond, namely, 1·13 A. Similar resonating states apparently take part in the structure of carbon oxysulphide and of carbon disulphide,[68] although there is less tendency for the formation of the $^{-}C\equiv\overset{+}{S}$ bond, than for the corresponding oxygen link.

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[63] L. O. Brockway, *J. Amer. Chem. Soc.*, 1936, **58**, 2516.

[64] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 860; see also N. V. Sidgwick, *Trans. Faraday Soc.*, 1934, **30**, 801.

[65] R. W. Dornte, *J. Amer. Chem. Soc.*, 1933, **55**, 4126.

[66] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336; the results differ from those given by L. Hengstenberg and L. Brú, *loc. cit.*, ref. (31).

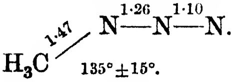
[67] For summary, see H. P. Klug, *loc. cit.*, ref. (41), p. 750.

[68] J. M. Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106.

[69] P. C. Cross and L. O. Brockway, *J. Chem. Physics*, 1935, **3**, 821.

[70] L. Pauling, *loc. cit.*, ref. (30).

The length of the C—H bond as used by different authors varies from 1·06 to 1·10 A. in aliphatic[4, 37, 55, 64] and from 1·06 to 1·14 A. in aromatic substances;[18, 25, 64] the additive distance is at least 1·06 A., and agreement between the results is as good as could be expected, especially as the electron scattering of the hydrogen atom is so small that it is frequently neglected (p. 72).

Molecular configurations. Electron-diffraction measurements have been applied in a number of different ways to throw light on the structures of various molecules. The diffraction pattern of methyl azide vapour is quite incompatible with a ring structure for the azide group, and a linear structure is indicated:[64] the configuration and distances in A. favoured may be represented by 

This structure is taken to imply resonance between the forms $-N=\overset{+}{N}=\overset{-}{N}$ and $-\overset{-}{N}-\overset{+}{N}\equiv N$, for the two nitrogen–nitrogen bond distances would then approach the values for N=N, *i.e.*, 1·26 A., and N≡N, *i.e.*, 1·10 A., respectively. The nitrogen valency angle of 135° ± 15° is in reasonable agreement with the value of 125° to be expected for a tetrahedral nitrogen atom. Striking confirmation of the proposed structure for the azide group has been obtained from *X*-ray measurements on crystalline cyanuric azide;[71] the azide group is found to be linear, as in alkali azides, the bond distances between successive nitrogen atoms being 1·26 A. and 1·11 A. respectively. The nitrogen bond angle is, however, stated to be 114°, and the C–N distance is given as 1·38, compared with 1·47 A. indicated by bond additivity.

The commonly written ring structure for diazomethane is rejected from an examination of the electron-diffraction pattern given by the vapour;[14] the carbon–nitrogen and nitrogen–nitrogen distances of 1·34 and 1·13 A. suggest resonance between the structures $H_2C=\overset{+}{N}=\overset{-}{N}$ and $H_2\overset{-}{C}-\overset{+}{N}\equiv N$. As might be expected, azomethane is a conventional azo-compound,[14] $CH_3{\cdot}N=N{\cdot}CH_3$, the methyl groups being in the *trans*-position; this formulation is compatible with the small dipole moment of *pp'*-dibromoazobenzene. The *cis*- and *trans*-forms of other substances, *e.g.*, Δ^2-butenes and βγ-epoxybutanes,[60] have been distinguished by means of electron-diffraction measurements.

The carbon–oxygen and carbon–carbon distances in carbon suboxide[14, 64] have been given as 1·18—1·20 A. and 1·27—1·30 A. respectively, whereas the normal formula $O{:}C{:}C{:}C{:}O$ would require the double-bond values of 1·28 and 1·38 A. This result is interpreted

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[71] (Miss) I. E. Knaggs, *Proc. Roy. Soc.*, 1935, *A*, **150**, 576.

as implying resonance between the normal state and two excited structures $\overset{+}{O}\equiv C—C\equiv C—\overset{-}{O}$ and $\overset{-}{O}—C\equiv C—C\equiv \overset{+}{O}$, so that all the bond distances would approach the values for trebly-bound atoms.

Early work[72] on cyanogen and diacetylene indicated a non-linear structure for these molecules, but later study[62] has shown this conclusion to be incorrect, a result in harmony with ordinary stereochemical considerations. The diffraction pattern for cyanogen agrees with a carbon–nitrogen distance of 1·16 A., the same as the accepted additive value for the $C\equiv N$ bond, but the carbon–carbon distance is only 1·43 A., which is somewhat closer to that for $C=C$ than for $C—C$. This suggests that the normal state of cyanogen, $N\equiv C—C\equiv N$, which is the most important, is in resonance with other states, *e.g.*, $\overset{-}{N}=C=C=\overset{+}{N}$ and $\overset{+}{N}=C=C=\overset{-}{N}$, containing doubly-bound carbon atoms. It is of interest to record here that the terminal carbon–nitrogen distances in methyl cyanide and *iso*cyanide have been found to be almost identical[63] (1·16 A.), thus providing strong evidence for the view that the form $R\cdot\overset{+}{N}\equiv\overset{-}{C}$ is an important contributor to the structure of *iso*cyanides. The structure of diacetylene is believed to be analogous to that of cyanogen: the carbon–carbon distances at the two ends of the molecule are 1·21 A., as expected for the $C\equiv C$ bond.[62] The distance between the central carbon atoms is, as with cyanogen, 1·43 A., a result implying resonance, to some extent, of the normal structure $H\cdot C\equiv C—C\equiv C\cdot H$ with the excited states $H\cdot\overset{+}{C}=C=C=\overset{-}{C}\cdot H$ and $H\cdot\overset{-}{C}=C=C=\overset{+}{C}\cdot H$.

Electron-diffraction results are incapable of distinguishing[73] between the structures of NNO and NON for nitrous oxide, because of the small difference in the scattering powers of oxygen and nitrogen atoms, but the first of these formulæ is generally favoured as being in harmony with the chemical properties, spectrum, and dipole moment. The extreme nitrogen–oxygen distance is found[73] to be 2·38 ± 0·06 A., which is in fair agreement with the sum of the bond distances for $N\equiv N$, *i.e.*, 1·10 A., and $N=O$, *i.e.*, 1·22 A., and also corresponds with the known moment of inertia of the molecule. The interpretation[70, 74] of this result is that in nitrous oxide there is resonance between $\overset{-}{N}=\overset{+}{N}=O$ and $N\equiv\overset{+}{N}—\overset{-}{O}$. The third possible state $\overset{--}{N}—\overset{+}{N}\equiv\overset{+}{O}$ is definitely excluded since this would reduce the shorter nitrogen–oxygen distance to 1·07 A., and the extreme distance would be 0·21 A. less than actually observed.

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[72] R. Wierl, *loc. cit.*, ref. (59).

[73] L. R. Maxwell *et al.*, *loc. cit.*, ref. (17).

[74] L. Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 498.

The electron-diffraction patterns of nitrogen dioxide, tetroxide, and pentoxide have also been examined, but the results are not sufficiently precise to permit of an unequivocal interpretation :[73] it is certain, however, that the linear model for nitrogen dioxide is not correct, the nitrogen valency angle being between 90° and 120°.

The evidence for the planar configuration of benzene is so overwhelming that there is little need for further confirmation : it is satisfactory to note, however, that the scattering of electrons by benzene derivatives can only be accounted for on this basis.[10, 18, 24, 44] The compound $B_3N_3H_6$, known as boron amide, gives an electron-diffraction pattern similar to that of benzene, and the molecule is evidently a flat, regular hexagon with alternate boron and nitrogen atoms round the ring.[75] The boron–nitrogen distance is uniformly 1·47 ± 0·07 A., which is much smaller than that required for the singly-linked B—N bond, *viz.*, 1·59 A., but reasonably close to the B=N value, 1·43 A.; it is probable that in boron amide, as in benzene, there is resonance between two alternative structures of the Kekulé type, so that all the boron–nitrogen bonds are effectively double. Mention may be made of the fact that *X*-ray diffraction measurements of crystalline cyanuric triazide [54] indicate that in the cyanuric ring alternate carbon–nitrogen distances are 1·38 and 1·31 A., corresponding approximately to the C—N and C=N bond values, 1·47 and 1·32 A., respectively; in spite of the apparent similarity to benzene and to boron amide, there is in this case evidently no resonance, the single and double bonds occupying fixed positions. Electron-diffraction measurements have been used to determine the structure of pentaborane, B_5H_9 [76]; it appears to consist of a square four-membered ring, made up of three BH_2 groups and a boron atom, the fifth boron group, as BH_3, being attached to the latter, almost coplanar with the ring.

The structure of nickel carbonyl, $Ni(CO)_4$, presents an interesting problem which has now been solved by means of electron diffraction. The dipole moment of this compound is zero, so that it is not cyclic, as had been suggested, but the four CO groups must either be at the corners of a square, that is planar, or else arranged tetrahedrally. The diffraction pattern definitely favours the latter structure,[77] in agreement with Pauling's views. The carbon–oxygen distance is 1·15 A., which is close to the value in carbon monoxide and to that expected for the C≡O bond; hence the triply linked carbonyl structure probably predominates in nickel carbonyl, as it appears to do in carbon monoxide. Paraldehyde has been shown to con-

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[75] A. Stock and R. Wierl, *Z. anorg. Chem.*, 1931, **203**, 228.

[76] S. H. Bauer and L. Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 2406.

[77] L. O. Brockway and P. C. Cross, *J. Chem. Physics*, 1935, **3**, 829.

sist of a staggered six-membered ring of alternate oxygen and carbon atoms : the angles are all approximately tetrahedral.[15, 78]

Valency angles. Measurements with carbonyl chloride and bromide [65] are in harmony with an angle of 110° ± 5° between the two carbon–halogen bonds in each case; the same result was found for the angle between the carbon–carbon and carbon–halogen bonds in acetyl chloride and bromide.[65] The experimental value is close enough to 109° to confirm the tetrahedral configuration of the carbon atom concerned; the value of 125° ± 10° found for the angle between the C=O and the other bonds also provides support for this arrangement.[65, 34] The angles between the C—Cl bonds in methylene chloride and in chloroform were at one time believed to be markedly in excess of the tetrahedral value :[10, 79] more recent work [55] has shown these results to be in error, and it now appears that the angles are 111° ± 2°.

The oxygen bond angle in chlorine monoxide [55] is 111° ± 2°, and in oxygen fluoride [14, 55] it is somewhat less, 105° ± 5° or 100 ± 3°; in dimethyl ether [55, 80] the oxygen angle is 111° ± 4°, allowing for free rotation of both methyl groups about the C—O bonds, and a closely similar result has been obtained with α-methylhydroxylamine.[34] These results might at first sight be taken as supporting the tetrahedral value as the natural oxygen valency angle, but this conclusion may not be justified. The distance between the chlorine atoms in chlorine monoxide, 2·82 A., is appreciably less than the normal distance of closest approach of two non-bonded chlorine atoms,[81] *viz.*, 3·7 A.; similarly in dimethyl ether the carbon atoms are only 2·39 A. apart, although the minimum distance of approach of non-bonded atoms [82] is normally 3·4 A. It is evident that in both these compounds there must be considerable repulsion between the chlorine atoms and the methyl groups, respectively, so that the observed valency angles may well be greater than the " natural " value. It may be noted that the approach of the methyl groups in dimethyl ether is not sufficient to interfere with free rotation, even after allowing an envelope 0·5 A. thick [83] round each hydrogen atom. The oxygen angle in dioxan is stated to be 110° ± 5°, and the same factor of repulsion of the groups attached to the oxygen atom arises here as with the compounds just considered. The

[78] D. C. Carpenter and L. O. Brockway, *loc. cit.*, ref. (57).

[79] L. Bewilogua, *Physikal. Z.*, 1931, **32**, 865.

[80] The value given by L. Brú, *Anal. Fis. Quim.*, 1932, **30**, 486, is probably incorrect.

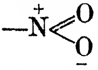
[81] R. G. Dickinson and C. Billicke, *J. Amer. Chem. Soc.*, 1928, **50**, 764; M. L. Huggins, *Chem. Reviews*, 1932, **10**, 447.

[82] S. B. Hendricks, *ibid.*, 1931, **7**, 430.

[83] N. V. Sidgwick, *Ann. Reports*, 1932, **29**, 70.

observations with dioxan show that in the vapour state, at least, the **Z**, or *trans*-, form predominates; this configuration agrees with the zero dipole moment of the liquid. In *pp*′-di-iododiphenyl ether the oxygen valency angle,[16] according to electron-diffraction results, is 118° ± 3°; as previously indicated,[84] a larger angle than in aliphatic ethers is not unreasonable. The ordinary method for interpreting electron-diffraction data does not permit of a determination of the configuration of sulphur dioxide with sufficient certainty to give the sulphur valency angle,[69] but by means of the radial distribution method the distance between the two oxygen atoms, as well as between sulphur and oxygen, can be evaluated, at least approximately. The results indicate an angle of 124° ± 15°,[28] in agreement with the value obtained from Raman and infra-red spectra. This angle and the sulphur–oxygen distance suggest that in sulphur dioxide there are at least two resonating structures, *viz.*, $\overset{-}{O}-\overset{+}{S}=O$ and $\overset{-}{O}=\overset{+}{S}-O$. In sulphur vapour itself, containing complex molecules, the sulphur angle is about 100°.[85]

Apart from the uncertain interpretation of the observations on methyl azide (p. 81) and on azomethane, which suggest a value greater than the tetrahedral, there is no definite quantitative evidence from electron scattering concerning the valency angle of tervalent nitrogen ; in PCl_3, PF_3, and $AsCl_3$, however, the angles are 100° ± 2°, 99° ± 4° and 101° ± 4°, respectively.[22] According to calculations by wave mechanics,[86] the bond angles in nitrogen and its congeners in the tervalent state should lie between 90° and 109° 28′, the former value being approached as the atomic weight increases; the results quoted above are in general agreement with this expectation, since there is reason to believe that the nitrogen angle is close to the tetrahedral value.[87] In nitromethane the valency angle has been found to be 127° ± 3°; [34] this is in harmony with the structure



$-\overset{+}{N}\genfrac{}{}{0pt}{}{\diagup\!\!\!\!\diagup O}{\diagdown \underset{-}{O}}$ as one of the resonating forms of the nitro-group, the nitrogen, in the quadrivalent state, being tetrahedral.

S. G.

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[84] *Ann. Reports*, 1935, **32**, 132.

[85] L. R. Maxwell, V. M. Mosley, and S. B. Hendricks, *Physical Rev.*, 1936, **50**, 41.

[86] L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

[87] See, *e.g.*, R. B. Barnes, W. S. Benedict, and C. M. Lewis, *Physical Rev.*, 1934, **45**, 347.

5. CHEMICAL KINETICS.

Though numerous ideas in the subject of chemical kinetics have been profitably pursued again during the current year, we must restrict attention in the present report to the major developments in the study of thermal reactions in homogeneous systems. The year has witnessed important advances in theory and an increased rate of accumulation of experimental material.

The Quantal Theory of Chemical Change.[1]

The quantal theory of chemical change, which was briefly outlined in last year's report,[2] has been in itself refined and elaborated by thermodynamic [3, 4] and statistical [5, 6] methods, and has been applied with marked success to a number of diversified problems, including diabatic unimolecular transformations,[7] ternary atomic collisions,[8] calculation of the energy of triatomic systems,[9, 5] reactions between hydrogen atoms and molecules,[10, 5] reactions between hydrogen and the halogens,[11] the ortho-para conversion of hydrogen under the influence of α-particles,[12] the radiochemical synthesis of hydrogen bromide,[13] reactions involving four atoms,[14] and the addition of atomic and molecular halogens to ethylene and its derivatives.[15] That the theory is capable of accommodating such diversity without distortion of its general features is in itself significant.

The object of the quantal theory of chemical change is an ambitious one, namely, to predict the absolute magnitude of the velocity of chemical reactions of all kinetic orders in homogeneous and heterogeneous systems. Though still in its infancy, it may be said to have succeeded, at least as far as elementary chemical changes are concerned. Its present protases will doubtless be

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[1] We adopt the words "quantal" and "quantally," following the suggestions of C. G. Darwin (*Nature*, 1936, **138**, 908), instead of the cumbrous "quantum-mechanical," etc.

[2] E. A. Moelyn-Hughes, *Ann. Reports*, 1935, **32**, 89.

[3] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1333.

[4] W. H. Rodebush, *J. Chem. Physics*, 1936, **4**, 744.

[5] L. Farkas and E. Wigner, *Trans. Faraday Soc.*, 1936, **32**, 708.

[6] H. Eyring and numerous collaborators (*vide infra*).

[7] A. E. Stearn and H. Eyring, *J. Chem. Physics*, 1935, **3**, 778.

[8] H. Eyring, H. Gershinowitz, and C. E. Sun, *ibid.*, p. 786.

[9] J. Hirschfelder, H. Eyring, and N. Rosen, *ibid.*, 1936, **4**, 121.

[10] J. Hirschfelder, H. Eyring, and B. Topley, *ibid.*, p. 170.

[11] A. Wheeler, B. Topley, and H. Eyring, *ibid.*, p. 178.

[12] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *ibid.*, p. 479.

[13] *Idem*, *ibid.*, p. 570.

[14] W. Altar and H. Eyring, *ibid.*, p. 661.

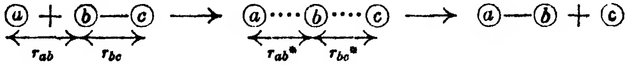
[15] A. Sherman, O. T. Quimby, and R. O. Sutherland, *ibid.*, p. 732.

replaced by others less drastic, but there can be no doubt that its fundamental conception constitutes a permanent acquisition to the science of chemical dynamics. The theory treats the approach of reactant molecules, their interaction during chemical change, and their separation thereafter as a continuous process, depicted by the movement, in phase space, of the representative point for the system. Occurrence of chemical change coincides with the passage of this point over an energy barrier, the height of which corresponds, roughly, with the energy of activation. Experiment demands that the velocity of chemical change shall generally be expressible as the product of two terms [equation (1)], of which the first, if not absolutely independent of temperature, is far less dependent upon it than is the second term:

$$k^* = A \,.\, e^{-E_A/RT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The problem thus resolves itself into a determination of the two quantities, A and E_A, which, although not strictly separable, may conveniently be treated as if they were. E_A must be evaluated quantally, A either quantally or classically according to circumstances. A is determined by the average velocity with which the representative point surmounts the col.

The quantal theory of reaction velocity has been applied in detail to reactions between two atoms, reactions between atoms and diatomic molecules, and to reactions between two diatomic molecules. In order to illustrate the principles involved, we shall select for discussion a reaction of intermediate complexity, namely, that occurring between an atom, a, and a diatomic molecule, bc:



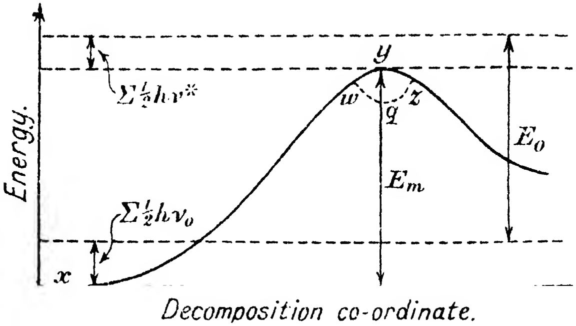
The method of determining the height, E_m, of the pass was outlined in last year's report.[2] It is due to H. Eyring and M. Polanyi,[16] whose treatment we have now to reconsider, paying attention to some of its finer points. For generality, rectangular co-ordinates must be replaced by co-ordinates inclined at an angle ϕ, such that

$$\sin \phi = - \{m_a m_b/(m_a + m_b)(m_b + m_c)\}^{\frac{1}{2}} \quad . \quad . \quad (2)$$

The resulting model enables us to represent the potential energy of the triatomic system, pictorially at least, as a function of a special spatial co-ordinate, which is usually termed the reaction path (see figure). Now the height (E_m) of the summit is the difference between the potential energies of the reactants (at the point x) and the activated complex (at the point y), both being, of course,

[16] *Z. physikal. Chem.*, 1931, *B*, **12**, 279.

static values. According to the quantal theory, both systems possess residual energies, which, at the absolute zero of temperature, are $\Sigma\frac{1}{2}h\nu_0$ and $\Sigma\frac{1}{2}h\nu^*$ respectively. If, therefore, we choose to define our energy of activation (E_0) as the difference between the actual energies of reactant and activated systems at $T = 0$, we have the relation



$$E_0 = E_m - (\Sigma\tfrac{1}{2}h\nu_0 - \Sigma\tfrac{1}{2}h\nu^*) \quad . \quad . \quad . \quad . \quad (3)$$

Of the quantities in this equation, ν_0 and E_0 are known experimentally from spectroscopic and kinetic data respectively; E_m and ν^* may be calculated from the theory under discussion.

Since activated complexes usually contain an odd number of electrons and are not molecules in the ordinary sense, the vibration frequencies which characterise their internal motions are not amenable to direct measurement, but must be obtained by indirect means. The method commonly adopted[16, 17, 18, 8, 11, 5] is a direct application of the classical equations of motion to the movement of a point particle in the neighbourhood of the col, where the force field is assumed to be expressible by a function of the form

$$\delta V = \tfrac{1}{2}[f_1(\delta r_{ab})^2 + f_2(\delta r_{bc})^2 + f_\alpha(\delta\alpha)^2] \quad . \quad . \quad . \quad (4)$$

In this equation, δ denotes the small difference produced in the potential energy (V), in the interatomic separations (r_{ab} and r_{bc}) and in the deformation angle (α) for systems displaced very slightly from the equilibrium system, for which $V = E_m$; $r_{ab} = r^*_{ab}$; $r_{bc} = r^*_{bc}$; $\alpha = 0$. The desired frequencies may be calculated from a knowledge of the masses and of the force constants (f). An important distinction is afforded by this analysis between the behaviour of normal triatomic molecules and activated triatomic complexes, since one of the f values for the latter is negative, with

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[17] H. Pelzer and E. Wigner, *ibid.*, 1932, *B*, **15**, 445.

[18] Cf. the treatment of stable triatomic systems, discussed by W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156**, 654.

the result that one of the frequencies of transverse vibration (which we shall call ν_-) has an imaginary value. The frequency of deformation (ν_a) and the frequency of the other transverse motion (ν_+) have real values for complexes as for normal molecules.

In order to illustrate the principles involved, we shall consider the specific example discussed in last year's Report,[2] attempting, at the same time, to show the relation of the new theory to the old, and of both to the facts.

The Kinetics of the Reaction $Br + H_2 \longrightarrow BrH + H$.—(1) *Experimental facts.* The results of M. Bodenstein and S. C. Lind [19] yield the following values for the constants of equation (1) :— $A = 1{\cdot}20 \times 10^{-10}$ c.c. per molecule-second; $E_A = 17{,}640$ cals./g.-mol. Extending the temperature region, and employing a totally different technique, F. Bach, K. F. Bonhoeffer, and E. A. Moelwyn-Hughes [20] found $A = 1{\cdot}17 \times 10^{-10}$ and $E_A = 17{,}740$, thus fully substantiating the earlier work. In round figures, therefore, and for the temperature region $T = 576° \pm 75°$ Abs., A has a value of $1{\cdot}2 \times 10^{-10}$ and E_A of 17,700 in these units.

(2) *Classical interpretation.* According to the collision theory in its simplest form, the rate of reaction is equated to the fraction of the total number of collisions for which the energy exceeds a critical value E, the theoretical expression for the velocity constant being $k^* = (r_a + r_{bc})^2(8\pi kT/\mu)^{\frac{1}{2}}e^{-E/RT}$. It follows that $E_A = E - \frac{1}{2}RT$; hence the kinetic value of $(r_a + r_{bc})$ is 1·57 A. In this manner, M. Trautz [21] found values of the same reasonable order of magnitude for the present reaction and for many others, thus establishing the classical collision theory for gases. If we regard the energy of activation as a critical value of the component of the relative kinetic energy referred to the line of centres,[22] we may proceed one stage further along classical lines. The above theoretical expression must now be multiplied by the factor $(1 + E/RT)$, so that, to within less than 3%, $E = E_A + \frac{1}{2}RT$. Solving for $(r_a + r_{bc})$ now gives us the value 0·38 A., showing that the greater the imposed restriction on the direction of approach, the smaller becomes the target area derived from kinetic measurements. Hence the classical interpretation is consistent, though inadequate.

(3) *Quantal interpretation.* With a constant resonance factor of 0·14, we have seen [2] that $E_m = 22{,}100$ cals. For the sake of simplicity, we now assume a strictly linear structure for the three atoms throughout the chemical change, *i.e.*, we take f_a of equation

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[19] *Z. physikal. Chem.*, 1906, **57**, 168.

[20] *Ibid.*, 1934, *B*, **27**, 71.

[21] *Z. anorg. Chem.*, 1916, **96**, 1.

[22] R. C. Tolman, "Statistical Mechanics," New York, 1927.

(4) as zero. We then find $\frac{1}{2}h\nu_+ = 2{,}730$ and $-\frac{1}{2}ih\nu_- = 160$; $\frac{1}{2}h\nu_{bc}$ is known to be 6,180 cals./g.-mol. Hence, by equation (3), $E_0 =$ 18,650 cals., which, though not directly comparable with E_A, lies very near to it. From the imaginary frequency ν_-, we may estimate the value of E. Wigner's factor,[23] for quantal transits ("tunnelling"), which is $[1 - \frac{1}{6}(\frac{1}{2}h\nu_-/kT)^2] = 1{\cdot}0052$. The correction thus amounts in the present case to about 0·5%, and can be ignored.

The application [10, 11] of H. Eyring's general formula[24] to the present case gives results in agreement with previous treatments,[17, 5] and proceeds as follows. The formula for the velocity constant is

$$k^* = \kappa \,.\, \frac{\sigma_{bc}}{\sigma_{abc}} \,.\, \frac{F_{abe}}{F_a F_{bc}} \,.\, e^{-E_0/KT} \,.\, v^* \quad . \quad . \quad . \quad (5)$$

The transmission coefficient (κ) is the average value of the absolute probability that the representative point, having reached the col, shall pass over it; its maximum value, according to classical theory, is 1/2. Leakage through the potential barrier may increase κ by an amount given approximately by the Wigner factor. σ is a symmetry term, which is integral for both reactant and activated systems. In the following account, we shall include all these factors in the term κ^*, which must be of the order of magnitude of unity. v^* is the average velocity of transit over the barrier, and will be given the classical value of $\sqrt{8kT/\pi\mu^*}$. The partition function, F_a, for the atom, a, is due entirely to translation, and is therefore $(2\pi m_a kT)^{3/2}/h^3$. The corresponding function for the molecule, bc, includes additional terms to account for rotation and quantised vibrations; F_{bc} is accordingly

$$\frac{[2\pi(m_b + m_c)kT]^{3/2}}{h^3} \,.\, \frac{8\pi^2 I_{bc} kT}{h^2} \,.\, (1 - e^{-h\nu_{bc}/kT})^{-1}$$

The nine degrees of freedom for the reactive complex, taken in order, are three for translation of the complex as a whole, two for rotations, one for the symmetrical transverse vibration, two for the degenerate deformation, and one for the relative translatory motion of the component parts of the decomposing complex, referred to the ordinate of decomposition. These motions, considered as separable, enable us to write

$$F_{abc} = \frac{[2\pi(m_a + m_b + m_c)kT]^{3/2}}{h^3} \,.\, \frac{8\pi^2 I_{abc} kT}{h^2} \,.\, (1 - e^{-h\nu_+/kT})^{-1} \times$$
$$(1 - e^{-h\nu_a/kT})^{-2} \,.\, \frac{(2\pi\mu^* kT)^{\frac{1}{2}}}{h}$$

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[23] *Z. physikal. Chem.*, 1932, *B*, **19**, 203.

[24] *J. Chem. Physics*, 1935, **3**, 107.

Substituting in equation (5), and combining the result with equation (3), we have the theoretical expression for the velocity constant

$$k^* = \kappa^* \cdot \left(\frac{h}{2\pi}\right)^2 \left(\frac{2\pi}{kT}\right)^{\frac{1}{2}} \left[\frac{m_a + m_b + m_c}{m_a(m_b + m_c)}\right]^{3/2} \frac{I_{abc}}{I_{bc}} \times \frac{\sinh \beta\nu_{bc}}{\sinh \beta\nu_+ \cdot \sinh^2 \beta\nu_a} \cdot e^{-Em/RT} \quad . \quad . \quad (6)$$

β is $h/2kT$. Comparison with equation (1) leads to the following relation [5] between the Arrhenius constant, E_A, and the height, E_m, of the mountain pass (N_0 being the Avogadro number) :

$$E_A = E_m - \tfrac{1}{2}RT - \tfrac{1}{2}N_0h\nu_{bc} \coth \beta\nu_{bc} + \tfrac{1}{2}N_0h\nu_+ \coth \beta\nu_+ + N_0h\nu_a \coth \beta\nu_a \quad . \quad . \quad (7)$$

Introducing the numerical values quoted above, we obtain the following theoretical results: $E_A = 18{,}090$ cals./g.-mol., and $A = 1{\cdot}11 \times 10^{-10}$ c.c. per molecule-second. Both are in good agreement with experiment.

A. Wheeler, B. Topley, and H. Eyring [11] have made calculations on the same reaction, assuming the resonance factor to be 0·20, and making allowance for the deformation of the triatomic system. The theoretical value of A [equation (1)] so obtained is $1{\cdot}06 \times 10^{-10}$, so that the quantal theory, like its classical predecessor, guarantees a fairly reasonable value for the collision frequency. The reason in both cases is to be traced to the high magnitude of interatomic repulsive forces at low separations. On the other hand, it is now found that $E_m = 25{,}100$ and that $h\nu_a = 1{,}309$ cals./g.-mol. Substituting into equation (7), the calculated value of the Arrhenius activation energy, E_A, becomes 23,630. Thus the present method of evaluating the energy of activation is sensitive to the proportion of the total potential energy which is ascribed to the Coulombic terms—which raises the following questions. Is the London procedure for estimating the potential energy of triatomic configurations in itself a sufficiently good approximation? Can we, as one of the authors asks, regard the existence of a dip round the col (shown by the dotted line *wqz* in the figure, p. 88) as a virtue or a defect in the Eyring–Polanyi theory? If the activated complex suffers marked bending, how far are we justified in constructing an energy surface in terms of only two spatial co-ordinates? While these and similar questions must await authoritative answers, the method may confidently be applied as a self-consistent, semi-empirical procedure, justified *a posteriori*.

Reactions in the Gaseous Phase.

Increasing attention is being paid to simple processes, especially those involving free atoms, and to the elucidation of the detailed simultaneous mechanisms which together are responsible for the net observed velocity of the decomposition of polyatomic molecules.

A. Farkas[25] has studied the exchange of hydrogen and deuterium atoms between the corresponding molecules and ammonia. The rate-determining step is $D + NH_3 \longrightarrow NH_2D + H$, for which $E_A = 11,000$, and the absolute rate is about 35 times as slow as that of the reaction $D + H_2 \longrightarrow DH + H$. The exchange reactions of water and of methane have similarly been investigated by A. Farkas and H. W. Melville.[26] W. Heller and M. Polanyi,[27] measuring the rate of reaction between sodium atoms and numerous inorganic halides, find an instructive parallelism between the velocity and the restoring force-constant as estimated from the Raman frequency of the halide molecule. E_A has a value of about 6,000 for the reaction[28] $O + O_3 \longrightarrow 2O_2$. Atomic mechanisms are very common in photochemical reactions, as for example, in the chlorine-sensitised oxidation of chloromethane, where the step $Cl + CH_2Cl_2 \longrightarrow HCl + CHCl_2$ has been detected.[29]

The reaction $D_2 + HCl \longrightarrow DH + DCl$ proceeds as a homogeneous bimolecular process,[30] with $E_A = 27,000$. Equally simple examples are afforded by the rate of formation[31] and decomposition[31a] of deuterium iodide, $D_2 + I_2 \rightleftarrows 2DI$. The data for these reactions are summarised in Table I.

M. Bodenstein and W. Kraus have made a complete study of the reaction of nitric oxide with oxygen, chlorine, and bromine molecules.[32] Essentially termolecular mechanisms control the reactions between nitric oxide and hydrogen,[33] and between oxygen atoms and molecules.[28] K. H. Geib's conclusion (1934) that most of the reactions undergone by the hydroxyl radical are termolecular has been confirmed by A. A. Frost and O. Oldenberg.[34]

The chain theory has again been applied to a number of reactions, including the oxidation of methane,[35] pentane,[36] acetylene,[37]

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[25] *J.*, 1936, 26.

[26] *Proc. Roy. Soc.*, 1936, *A*, **157**, 625.

[27] *Trans. Faraday Soc.*, 1936, **32**, 633.

[28] A. Eucken and F. Patat, *Z. physikal. Chem.*, 1936, *B*, **33**, 459.

[29] W. Brenschede and H. J. Schumacher, *ibid.*, 1936, *A*, **177**, 245.

[30] P. Gross and H. Steiner, *J. Chem. Physics*, 1936, **4**, 165.

[31] K. H. Geib and A. Lendle, *Z. physikal. Chem.*, 1936, *B*, **32**, 463.

[31a] J. C. L. Blagg and G. M. Murphy, *J. Chem. Physics*, 1936, **4**, 631.

[32] *Z. physikal. Chem.*, 1936, *A*, **175**, 294.

[33] C. N. Hinshelwood and J. W. Mitchell, *J.*, 1936, 378.

[34] *J. Chem. Physics*, 1936, **4**, 642.

[35] H. Sachsse, *Z. physikal. Chem.*, 1936, *B*, **33**, 229; W. A. Bone and J. B. Gardner, *Proc. Roy. Soc.*, 1936, *A*, **154**, 297; R. G. W. Norrish and S. G. Foord, *ibid.*, 1936, *A*, **157**, 503.

[36] A. Aivazov and M. Neumann, *Z. physikal. Chem.*, 1936, *B*, **33**, 319.

[37] E. W. R. Steacie and R. O. Macdonald, *J. Chem. Physics*, 1936, **4**, 75.

TABLE I.*

Reaction.	E_A for the H reaction.	$RT.\ln\frac{k_H}{k_D}\sqrt{\frac{\mu_H}{\mu_D}}$.	Reaction.	E_A for the H reaction.	$RT.\ln\frac{k_H}{k_D}\sqrt{\frac{\mu_H}{\mu_D}}$.
$H + H_2$	5,500[A]	1,050	$H + N_2O$	13,800[D]	0
$D + D_2$			$D + N_2O$		
$D + H_2$	4,850[A]	1,160	$D + NH_3$	10,800[26]	1,230
$D + D_2$			$H + ND_3$		
$Br + H_2$	17,700[20]	1,440	$H + PH_3$	14,400[E]	600
$Br + D_2$			$D + PH_3$		
$Cl + H_2$	*ca.* 6,000[B]	1,400	$H_2 + C_2H_4$	43,100[F]	1,490
$Cl + D_2$			$D_2 + C_2H_4$		
$Na + HCl$	6,100[C]	300	$H_2 + H_2 + NO$	45,000[33]	0
$Na + DCl$			$D_2 + D_2 + NO$		
$H_2 + I_2$	42,500[31]	580	$H + H + H$	0[G]	0
$D_2 + I_2$			$D + D + D$		
$HI + HI$	40,000[31a]	1,240			
$DI + DI$					

* After H. W. Melville, *Science Progress*, 1936, No. 123, p. 499.

A. A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1935, *A*, **152**, 124.
B. G. K. Rollefson, *J. Chem. Physics*, 1934, **2**, 144.
C. C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.*, 1935, **31**, 1932.
D. H. W. Melville, *J.*, 1934, 1243.
E. H. W. Melville and I. L. Bolland, *Proc. Roy. Soc.*, in press.
F. R. A. Pease and A. Wheeler, *J. Amer. Chem. Soc.*, 1936, **58**, 1665.
G. I. Amdur, *ibid.*, 1935, **57**, 856.

benzene,[38] methylamine,[39] and silane,[40,41,42] and the decomposition of alkali azides [43] and divinyl ether.[44]

Polymerisation processes formed the topic of a discussion organised by the Faraday Society. The kinetic aspects of the general treatment have been discussed by A. Abkin and S. Medvedev; C. E. H. Bawn, J. E. Carruthers, and R. G. W. Norrish; H. Dostal and H. Mark; K. Freudenberg; G. Gee; H. W. Melville and S. C. Gray; E. A. Moelwyn-Hughes; M. W. Perrin; E. K. Rideal; G. Salomon and W. F. K. Wynne-Jones.[45] The earlier theory of polymerisation reactions has been generally developed, and modified [46] to allow for the specific influence of promoters and inhibitors.

The decompositions of azomethane,[47] ethylene oxide,[48] ethyl-

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[38] R. H. Griffith and S. G. Hill, *Trans. Faraday Soc.*, 1936, **32**, 829.

[39] H. J. Emeléus and L. J. Jolly, *J.*, 1936, 1524.

[40] P. S. Schantarowitsch, *Acta Physicochim.*, *U.R.S.S.*, 1935, **2**, 673.

[41] H. Gutschmidt and K. Clusius, *Z. physikal. Chem.*, 1935, *B*, **30**, 265.

[42] H. J. Emeléus and K. Stewart, *J.*, 1935, 677.

[43] W. E. Garner and D. J. B. Marke, *J.*, 1936, 657.

[44] H. A. Taylor, *J. Chem. Physics*, 1936, **4**, 116.

[45] *Trans. Faraday Soc.*, 1936, **32**, pp. 1—412.

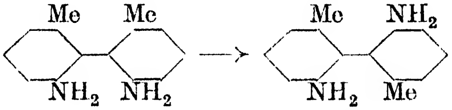
[46] G. Gee and E. K. Rideal, *ibid.*, p. 666; *Proc. Roy. Soc.*, 1936, *A*, **153**, 116.

[47] D. V. Sickman and O. K. Rice, *J. Chem. Physics*, 1936, **4**, 236.

[48] C. J. M. Fletcher and G. K. Rollefson, *J. Amer. Chem. Soc.*, 1936, **58**, 2129; R. V. Seddon and M. W. Travers, *Proc. Roy. Soc.*, 1936, *A*, **156**, 273; H. W. Thompson and M. Meissner, *Trans. Faraday Soc.*, 1936, **32**, 1451.

amine[49] and diethyl ether[50] have all been carefully re-examined under wide ranges of conditions. In connexion with the last reaction, L. A. K. Staveley and C. N. Hinshelwood[51] have determined the conditions under which nitric oxide may act either as a catalyst or as an inhibitor. The reaction $F_2O_2 \longrightarrow F_2 + O_2$ proceeds by a simple unimolecular mechanism.[52] The kinetics of the decomposition of benzylideneazine and ω-azotoluene[53] yield values of E_A which are consistent with the greater stability of the azo-nitrogen bond, compared with the azine bond. The homogeneous unimolecular decomposition of silane[53a] is more consistent with the mechanism $SiH_4 \longrightarrow SiH_2 + H_2$, proposed by Kassel (1932), than with the mechanism $SiH_4 \longrightarrow SiH_3 + H$ anticipated by analogy from Rice and Dooley's work (1934). A common energy of activation has been found for the homogeneous unimolecular decomposition of *tert.*-butyl and *tert.*-amyl chlorides.[53b]

Two further examples may be added to the not very abundant information available[54, 2] on the direct experimental comparison between the kinetics of reactions in the gas phase and in solution. The unimolecular racemisation of 2 : 2′-diamino-6 : 6′-dimethyldiphenyl[55] has roughly the same velocity and the same E_A value in the homogeneous gas phase as in solution in diphenyl ether:



The same observation applies to the bimolecular addition of acraldehyde to *cyclo*pentadiene in the gas phase[56] and in benzene solution.[57]

Reactions in Solution.

The greater difficulties in the way of interpreting the kinetics of reactions in solution are to some extent offset by the greater

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[49] H. A. Taylor and J. G. Ditman, *J. Chem. Physics*, 1936, **4**, 212.

[50] E. W. R. Steacie, W. H. Thatcher, and S. Rosenberg, *ibid.*, p. 220; C. J. M. Fletcher and G. K. Rollefson, *loc. cit.*, ref. (48).

[51] *Proc. Roy. Soc.*, 1936, *A*, **154**, 335; *J.*, 1936, 812.

[52] P. Frisch and H. J. Schumacher, *Z. physikal. Chem.*, 1936, *B*, **34**, 322.

[53] G. Williams and A. S. C. Lawrence, *Proc. Roy. Soc.*, 1936, *A*, **156**, 444.

[53a] T. R. Hogness, T. L. Wilson, and W. C. Johnson, *J. Amer. Chem. Soc.*, 1936, **58**, 108.

[53b] D. Brearly and G. B. Kistiakowsky, *ibid.*, p. 43.

[54] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933.

[55] G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, 1936, **58**, 1042; cf. C. C. Li and R. Adams, *ibid.*, 1935, **57**, 1565; W. H. Rodebush, *J. Chem. Physics*, 1936, **4**, 744.

[56] G. B. Kistiakowsky and T. R. Lacher, *J. Amer. Chem. Soc.*, 1936, **58**, 123.

[57] A. Wassermann, *J.*, 1936, 1027.

wealth of experimental material. Unless we adopt a quasi-thermodynamic approach,[2, 3, 4, 58] we must be content with making step-wise progress, by examining, for example, reactions in groups, selected so as to reveal the effect of a single variable factor. When dealing with fairly complicated molecules, the homologous groups of organic chemistry are eminently suitable. On the other hand, a classification of chemical reactions based on the nature of the interatomic forces concerned [59] offers certain advantages.

In some respects, the simplest known reactions in solution are the bimolecular reactions between ions and polar molecules, most of which have normal velocities.[2, 54] Ogg and Polanyi's method for evaluating their energies of activation was described in the last report.[2] Further instances of great interest have been studied by E. D. Hughes, F. Juliusberger, A. D. Scott, B. Topley, and J. Weiss,[60] by E. Bergmann, M. Polanyi, and A. L. Szabo,[61] by D. P. Evans,[62] and by A. R. Olson and collaborators,[63] who have attempted an interpretation of the slight differences in P values for reactions involving halide ions in terms of their entropies of solution. J. W. Baker and W. S. Nathan have, independently, given a statistical explanation of the relative reactivities of halide and nitrate ions in terms of their shapes (spherical and planar, respectively), and of their absolute dimensions.[64] C. K. Ingold and W. S. Nathan,[65] in a study of the hydrolysis of esters, have chosen a series of reactions in such a way as to eliminate the direct electrostatic interaction between the hydroxyl ion and the carboxylic group, and to isolate the induced polar effects. For a series of *p*-substituted derivatives of ethyl benzoate, the P factor remains constant, while the absolute velocity varies by a factor of about 5,000, which is reflected in a change of E_A values amounting to 5,500 calories. The results are in good agreement with Nathan and Watson's rule.[66] The problem of hydrolysis has also been studied by W. B. S. Newling and C. N. Hinshelwood,[67] chiefly from the point of view of discovering the comparative behaviour of esters towards acid and basic attack. They find that a 10,000-fold change in k is to

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[58] E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, 1936, **32**, 1723.

[59] E. A. Moelwyn-Hughes and A. Sherman, *J.*, 1936, 101.

[60] *Ibid.*, p. 1173.

[61] *Trans. Faraday Soc.*, 1936, **32**, 843.

[62] *J.*, 1936, 785.

[63] A. R. Olson and F. A. Long, *J. Amer. Chem. Soc.*, 1936, **58**, 383; M. J. Young and A. R. Olson, *ibid.*, p. 1157.

[64] *J.*, 1936, 236.

[65] *Ibid.*, p. 222.

[66] Cf. C. N. Hinshelwood, *Ann. Reports*, 1933, **30**, 43.

[67] *J.*, 1936, 1357.

be attributed almost entirely to a change in E_A. It is noteworthy that $(E_{H^+} - E_{OH^-})$ in aqueous acetone seems to be about 1,000 calories less than in pure water.[68] Another interesting series of reactions which have been measured and discussed, by G. N. Burkhardt and collaborators,[69] is the hydrogen-ion catalysis of the hydrolysis of alkyl hydrogen sulphates. An isolated example of an unusual kind is afforded by Yun-Pu Liu and Tien-Chi Wei's study [70] of the rate of hydration of methylethylethylene under the influence of acids. A theory of reactions between ions and polar molecules has been advanced.[71]

Continued attention is being paid to the kinetics of reactions between two polar molecules. A. W. Chapman and F. A. Fidler [72] conclude, from a study of the effects of substituents on the Beckmann transformation of picryl ethers in carbon tetrachloride solution, that the change is an intramolecular conversion of a complex formed from the reactant and the catalyst. Cyclisation reactions have been studied in great detail by G. Salomon,[73] who resolves the semi-empirical term, P, into two factors, one of which is quantitatively related to the surface energy. This, in turn, is calculated from Langmuir's formula for capillary forces, which differ according to the geometric configuration of the halogeno-amine. Further examples of the Menschutkin reaction have also been examined by J. W. Baker,[74] by N. J. T. Pickles and C. N. Hinshelwood,[75] and by A. Singh and D. H. Peacock,[76] while the kindred change involved in sulphonium-salt formation has been studied by N. Hellström.[77]

The theory of reactions between ions in solution has been further developed,[78] yielding the following relations for the factor P and for the variation of E_A with temperature and with ionic strength:

$$\ln P = -\frac{z_A z_B \varepsilon^2 L}{kDr} + \frac{z_A z_B \varepsilon^2}{2DkT}(3LT - 1)\kappa$$

$$E_A = E - \frac{N_0 z_A z_B \varepsilon^2}{Dr}(LT - 1)(1 - \tfrac{3}{2}\kappa r)$$

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[68] Cf. Moelwyn-Hughes, *op. cit.*, p. 253.

[69] G. N. Burkhardt, W. G. N. Ford, and E. Singleton, *J.*, 1936, 17; G. N, Burkhardt, A. G. Evans, and E. Warhurst, *ibid.*, p. 25; G. N. Burkhardt, C. Horrex, and (Miss) D. I. Jenkins, *ibid.*, p. 1649.

[70] *J. Chinese Chem. Soc.*, 1936, **4**, 297.

[71] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, *A*, **157**, 667.

[72] *J.*, 1936, 448.

[73] *Trans. Faraday Soc.*, 1936, **32**, 153; *Helv. Chim. Acta*, 1936, **19**, 743.

[74] *J.*, 1936, 1448.

[75] *Ibid.*, p. 1353.

[76] *J. Physical Chem.*, 1936, **40**, 669.

[77] *Z. physikal. Chem.*, 1936, *A*, **177**, 337.

[78] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, *A*, **155**, 308.

Both equations are in substantial agreement with experiment, the former being capable of accounting for the extremely high (10^{+8}) and low (10^{-8}) values of P found when the charges of the reacting ions are unlike and like respectively.

The principles and method of the technique for measuring rapid reactions have been described in detail by F. J. W. Roughton and G. A. Millikan,[79] and have been applied by G. A. Millikan [80] to determine the rates of combination and dissociation of muscle hæmoglobin with oxygen and with carbon monoxide. H. von Halban and H. Eisner [81] have continued their investigation of inorganic reactions by the same method.

H. M. Dawson has extended his well-known work on individual catalytic coefficients to include the influence of temperature on the hydrolysis of aqueous solutions of monochloroacetate.[82] Different values of E_A have been found for the three simultaneous modes of decomposition of *iso*propyl bromide in alkaline solution, which, according to Ingold's theory, are denoted by the symbols S_N2 (bimolecular substitution), $E\,2$ (bimolecular elimination) and S_N1 (unimolecular dissociation).[83] A composite mechanism seems probable also in the acidolysis of numerous phenolic ethers, which have been studied by R. P. Ghaswalla and F. G. Donnan,[84] particularly in view of their discovery that the Arrhenius equation is not applicable to the pseudo-unimolecular constants obtained. Two modes of decomposition of the ether–hydrogen halide complex are thus postulated.

M. Buboux and R. Farre [85] have supplied further confirmation of Bredig and Fraenkel's standard work on the hydrogen-ion catalysis of diazoacetic ester. C. A. Marlies and V. K. LaMer [86] have added to our knowledge of the catalytic decomposition of nitroamine. Catalyses by hydrosulphide ions [87] and in sulphuric acid solution [88] have also been the subject of investigation. Among more complicated systems must be noted the reaction between ferric ions and the oxy-acids of nitrogen,[89] and between bromine and allyl alcohol.[90] E. F. Caldin and J. H. Wolfenden [91] have made

[79] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, *A*, **155**, 258.

[80] *Ibid.*, 1936, *B*, **120**, 366.

[81] *Helv. Chim. Acta*, 1936, **19**, 915.

[82] H. M. Dawson and E. R. Pycock, *J.*, 1936, 153.

[83] E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *J.*, 1936, 225.

[84] *Ibid.*, p. 1341.

[85] *Helv. Chim. Acta*, 1936, **19**, 1177.

[86] *J. Amer. Chem. Soc.*, 1935, **57**, 1812.

[87] E. Friedmann, *J. pr. Chem.*, 1936, **146**, 179.

[88] H. C. S. Snethlage, *Rec. trav. chim.*, 1936, **55**, 712, 874.

[89] E. Schröer, Akademische Verlagsgesellschaft, Leipzig, 1936.

[90] M. Schar and L. C. Riesch, *J. Amer. Chem. Soc.*, 1936, **58**, 667.

[91] *J.*, 1936, 1239.

an interesting study of the cyclisation of a charged molecule. R. Livingston and E. A. Schoeld[92] have confirmed the work of Livingston and Bray (1923) on the reaction between bromine and hydrogen peroxide, and have demonstrated the absence of a chain mechanism.

The Influence of Pressure on the Velocity of Reactions in Solution.

The quasi-thermodynamic treatment of reaction velocity was given first by J. H. van't Hoff.[93] Within the restricted limits imposed by the suppositions underlying the treatment, it can be shown that, just as the increase (ΔH) in heat content between passive and active molecules may be found from the temperature variation of k, so may the increase (ΔV) in volume between passive and active molecules be found from the pressure variation of k. The values of the term ΔV given in the table have been calculated directly[58] by means of the equation $d\ln k/dp = - \Delta V/RT$, from

Reaction.	Solvent.	ΔV, c.c./g.-mol.
Hydrolysis of methyl acetate, catalysed by N-HCl	Water	$-$ 9·0
Hydrolysis of sucrose, catalysed by N-HCl	Water	$+$ 2·7
Reaction between acetic anhydride and ethyl alcohol	Ethyl alcohol	$-$ 16·5
,, ,, ,, ,,	Toluene	$-$ 12·5
,, ,, ,, ,,	Hexane	$-$ 4·16

the early data quoted by van't Hoff, and from the recent and more extensive data obtained by E. G. Williams, M. W. Perrin, and R. O. Gibson.[94]

Reactions involving Deuterium in Solution.

T. M. Lowry[95] proposed the name "prototropy" to describe chemical changes which may be represented by the migration of a proton. Hydrolytic reactions in general come under this category, as do also catalyses by acids and bases. Hydrolyses are among the most studied and least understood of chemical changes. The discovery of deuterium quickened general interest in the problem, and, although relatively little quantitative work has yet been carried out on deuterolysis,[96] it is quite clear that the new isotope is to be

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[92] *J. Amer. Chem. Soc.*, 1936, **58**, 1244.

[93] "Vorlesungen über theoretische und physikalische Chemie," Vol. 1, p. 236, Braunschweig, 1901; cf. refs. 2, 6, and 58.

[94] *Proc. Roy. Soc.*, 1936, *A*, **154**, 684.

[95] *Chem. Reviews*, 1927, **4**, 231.

[96] Following K. F. Bonhoeffer (see below), we shall adopt the terms protolysis and deuterolysis for reactions wherein the molecules H_2O and D_2O, respectively, are participating.

regarded more as a useful tool than as a golden key. We shall therefore refer only to some of the established experimental facts.

When aliphatic compounds are dissolved in heavy water, there occurs a ready exchange between the deuterium atoms of the solvent and hydrogen atoms of the solute. M. Harada and T. Titani[97] have confirmed the findings of Bonhoeffer and Brown (1933) on the exchange of deuterium atoms between D_2O and certain hexoses. After establishment of equilibrium, the distribution coefficient of deuterium atoms between solute and solvent is 0·87—0·70 in the case of acetone,[98] 0·88 for acetylacetone,[99] and 0·78 for nitromethane.[1] The hydroxyl ion is often found to induce, or at least to accelerate, the exchange. Thus K. Wirtz and K. F. Bonhoeffer[2] find that the hydrogen atoms in the hydrogen molecule exchange with the deuterium atoms of heavy water in the presence of alkali at 100°. They formulate the following mechanism, in conformity with the Lowry–Brönsted definition of bases as proton-acceptors:

$$\boxed{\mathrm{DO^- + H}}\!-\!\boxed{\mathrm{H + D}}\mathrm{OD} \longrightarrow \mathrm{DOH + H{-}D + OD^-}$$

Were all the deuterium atoms replaced by protium atoms, the change would be described as the alkaline hydrolysis of the hydrogen molecule. Other solutes for which exchange has been either attempted or effected are chloroform,[3] the dihydroxybenzenes,[4] and formaldehyde.[5]

The ionic product of D_2O in the neighbourhood of 25° has been determined electrometrically by W. F. K. Wynne-Jones,[6] whose results, which confirm the earlier value given by E. Abel, E. Bratu, and O. Redlich[7] at 21°, are given in the following form:

$$(\mathrm{H_2O});\quad -\log_{10} K = 14{\cdot}00 - 0{\cdot}0331\,(t^\circ - 25) + 0{\cdot}00017(t^\circ - 25)^2$$
$$\Delta H = 13{,}450 - 42{\cdot}8\,(t^\circ - 25)$$
$$(\mathrm{D_2O});\quad -\log_{10} K = 14{\cdot}71 - 0{\cdot}0354\,(t^\circ - 25) + 0{\cdot}00017\,(t^\circ - 25)^2$$
$$\Delta H = 14{,}420 - 42{\cdot}8\,(t^\circ - 25)$$

The quantity $\Delta H_1 - \Delta H_2$ is thus 970 calories. At 25°, we have $K_{H_2O} = [H^+][OH^-] = 1{\cdot}00 \times 10^{-14}$; $K_{D_2O} = [D^+][OD^-] = 1{\cdot}95 \times$

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[97] *Bull. Chem. Soc. Japan*, 1936, **11**, 55.

[98] R. Klar, *Z. physikal. Chem.*, 1934, *B*, **26**, 335; J. O. Halford, L. C. Anderson, J. R. Bates, and R. D. Swisher, *J. Amer. Chem. Soc.*, 1935, **57**, 1663.

[99] R. Klar, *loc. cit.*, ref. (98).

[1] O. Reitz, *Z. physikal. Chem.*, 1936, *A*, **176**, 363.

[2] *Ibid.*, **177**, 1.

[3] J. Horiuti and Y. Sakamoto, *Bull. Chem. Soc. Japan*, 1936, **11**, 627.

[4] F. K. Münzberg, *Z. physikal. Chem.*, 1936, *B*, **33**, 39.

[5] K. Wirtz and K. F. Bonhoeffer, *ibid.*, **32**, 108.

[6] *Trans. Faraday Soc.*, 1936, **32**, 1397.

[7] *Z. physikal. Chem.*, 1935, *A*, **173**, 353.

10^{-15} (mols./l.)^2. The equilibrium constant $K = [\text{EtOD}][\text{HOH}]/[\text{EtOH}][\text{HOD}]$ has the value 1·11 at 25°, and the rate at which the equilibrium is reached has also been determined.[8]

The principal kinetic data on reactions in deuterium oxide refer to the following changes.

(1) *Mutarotation of glucose, uncatalysed.* E. Pacsu[9] published the first datum on the velocity of chemical change in pure heavy water. It referred to an 18% solution of glucose at 20°, and, although the corresponding velocity in ordinary water under these conditions has not been measured, a sufficiently close estimate may be obtained by interpolation from the classical work of Hudson and Dale. The comparison yields a ratio $k_{D_2O}/k_{H_2O} = 0{\cdot}328$. In more dilute solutions of glucose in heavy water, a slightly lower value of 0·317 was found by E. A. Moelwyn-Hughes, R. Klar, and K. F. Bonhoeffer[10] to hold, within the limits of error, over a temperature range of 30°. Hence, there is no difference in the two E_A values. If, however, collisions between solute and solvent molecules determine the rate, both E_A values must be corrected for the temperature coefficient of the collision frequency, which has a different value for the two solvents. On the simplest basis, $E_{D_2O} - E_{H_2O}$ becomes 750 calories. These figures refer, of course, to velocities of mutarotation in the two pure media. For solvents of intermediate composition, it seems reasonable to ascribe catalytic efficiency to the molecule HOD also. To do so requires a knowledge of the equilibrium constant $K = [\text{HOD}]^2/[\text{HOH}][\text{DOD}]$, the values for which have been estimated by B. Topley and H. Eyring.[11] In this way, W. H. Hammill and V. K. LaMer[12] find k_{HOD} to have a value intermediate between those for k_{HOH} and k_{DOD}, while the ratio of the latter is concluded to be 1/0·263 at 25°.

(2) *Mutarotation of glucose, catalysed by protons and deuterons.* With hydrochloric acid as catalyst, the following values have been obtained for the ratio of the catalytic coefficients at various temperatures:[13]

t	9·00°	14·80°	20·69°	25·19°	30·39°	35·24°
$k_{D_3O^+}/k_{H_3O^+}$	0·53	0·56	0·63	0·64	0·68	0·77

(3) *Inversion of sucrose, catalysed by acids.* A ratio $k_{D_3O^+}/k_{H_3O^+}$ greater than unity holds for this reaction, and for a number of others, discussed below. With sulphuric acid as the source of

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[8] W. J. C. Orr, *Trans. Faraday Soc.*, 1936, **32**, 1033.
[9] *J. Amer. Chem. Soc.*, 1934, **56**, 745.
[10] *Z. physikal. Chem.*, 1934, *A*, **169**, 113.
[11] *J. Chem. Physics*, 1934, **2**, 381.
[12] *Ibid.*, p. 891.
[13] E. A. Moelwyn-Hughes, *Z. physikal. Chem.*, 1934, *B*, **26**, 272.

protons the ratio 1·66 was obtained[14] for $k_{D_3O^+}/k_{H_3O^+}$ at 40°, and an approximate value of 1·67 at 30·7°. B. Gross, H. Suess, and H. Steiner,[15] studying the same system, obtain a value nearer 2. The discrepancy may be due, as they note, to the difference in concentration of catalyst employed in the two cases. The dibasicity of the acid introduces complications which may be avoided by using HCl and DCl. With these catalysts,[13] the following figures are found :

t	18·71°	24·27°	30·02°	37·13°
$\alpha = k_{D_3O^+}/k_{H_3O^+}$	1·80	1·77	1·75	1·55

(4) *Hydrolysis of esters, catalysed by acids.* K. Schwarz[16] found that methyl and ethyl acetates were hydrolysed by acids about 50% more rapidly in heavy than in ordinary water. J. C. Hornel and J. A. V. Butler,[17] using sulphuric acid as catalyst, have found the ratios for the rates of deuterolysis and protolysis of methyl acetate to be $\alpha = 1{\cdot}85$ at 15° and $\alpha = 1{\cdot}68$ at 25°, in striking agreement with the data for the inversion of sucrose, and indicating that the term ΔE is mainly responsible for the difference in rates.

(5) *Decomposition of diazoacetic ester, catalysed by acids.* Again the heavy isotope has the faster velocity,[18] α being about 3.

(6) *Neutralisation of nitroethane.* A ratio of 1·5 holds for k_{OD^-}/k_{OH^-} in the case of the reaction between the two ions and nitroethane, and a ratio of 10 for the relative rates of reaction of the common ion OD^- with α-nitro- and with α-nitro-αα-dideutero-ethane.[19]

(7) *Enolisation of nitromethane.* According to Pedersen (1932), the rate of substitution of bromine in nitromethane is governed by the rate of conversion from the keto- to the enol form. Bromine and chlorine are introduced at the same rate, which is independent of their concentration and is proportional to that of any basic catalyst. The rate-determining step may thus be regarded as the rate of transference of a proton from the substrate to the base. O. Reitz[20] finds that, in water at 25°, nitromethane passes on its first proton to the acetate ion 6·5 times as rapidly as its trideutero-analogue passes on its first deuteron to the same base. Smaller values of the same ratio are found when the proton- or deuteron-acceptor is the water molecule or the monochloroacetate ion.

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[14] E. A. Moelwyn-Hughes and K. F. Bonhoeffer, *Naturwiss.*, 1934, **11**, 174.

[15] *Ibid.*, p. 662; *Trans. Faraday Soc.*, 1936, **32**, 883.

[16] *Anzeiger Akad. Wiss. Wien*, 1934, **26**, 4.

[17] *J.*, 1936, 1361.

[18] P. Gross, H. Steiner, and F. Krauss, *Trans. Faraday Soc.*, 1936, **32**, 877.

[19] W. F. K. Wynne-Jones, *J. Chem. Physics*, 1934, **2**, 381.

[20] *Z. physikal. Chem.*, 1936, *A*, **176**, 363.

(8) *Hydrolysis of the monochloroacetate ion.* The ratio k_{D_2O}/k_{H_2O} appears to be 1·2 in both ordinary and heavy water as media, but accurate analysis of the complete reaction presents certain difficulties.[21]

(9) *Hydrolysis of acetal and of ethyl orthoformate, catalysed by acids.* Hornel and Butler [17] find, for the two reactions respectively, the ratios $k_{D_3O^+}/k_{H_3O^+} = 2{\cdot}66$ and 2·05, both being independent of the nature of the buffer.

(10) *Biochemical processes.* Interesting information is accruing on the rate of growth of moulds in culture media containing D_2O, but we must be content with merely citing the references.[22]

Hypothetical energy differences which may be held responsible for the difference in rates are shown in the following table :

Catalysed reaction.		$RT \,.\, \ln k_H/k_D$ (cals./g.-mol.).
Mutarotation of glucose	at 15°	+ 325
	at 25°	+ 255
	at 35°	+ 180
Hydrolysis of sucrose	at 18°	− 340
	at 37°	− 270
Hydrolysis of methyl acetate	at 15°	− 360
	at 25°	− 280
Neutralisation of nitroethane		− 240
Hydrolysis of acetal		− 570
Hydrolysis of ethyl orthoformate		− 430

It may be noted that, if k were regarded as proportional to the viscosity of the medium, the energy terms would be small positive values, increasing with temperature at such a rate as to be comparable with the energy terms found for reactions in the gaseous phase at high temperatures.

The mechanism of proton transfer reactions has been discussed theoretically from very different standpoints.[23] In all discussions, however, the importance of Brönsted's empirical relation between catalytic coefficient and dissociation constant is fully appreciated.

The Frequency of Collisions in Liquid Systems.

In view of the forthcoming discussion which is being arranged by the Faraday Society on the kinetics of reaction in solution, it will

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[21] O. Reitz, *Z. physikal. Chem.*, 1936, *A*, **177**, 85.

[22] A. Farkas, L. Farkas, and J. Yudkin, *Proc. Roy. Soc.*, 1934, *B*, **115**, 373; B. Cavanagh, J. Horiuti, and M. Polanyi, *Nature*, 1934, **133**, 797; K. H. Geib and K. F. Bonhoeffer, *Z. physikal. Chem.*, 1936, *A*, **175**, 459; O. Reitz, *ibid.*, p. 257; F. Salzer and K. F. Bonhoeffer, *ibid.*, **176**, 202.

[23] J. Horiuti and M. Polanyi, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 505; R. P. Bell, *Proc. Roy. Soc.*, 1936, *A*, **154**, 414; E. A. Moelwyn-Hughes, *Acta Physicochim. U.R.S.S.*, 1936, **4**, 173; J. C. Hornel and J. A. V. Butler, *loc. cit.*, ref. (17).

serve no useful purpose to enter into any detail on this highly complicated problem. Mention must be made, however, of the continued attention which has been paid to it during the present year,[24] and to the desirability, well exemplified by the work of W. A. Waters,[25] of applying as many of the formulæ as are extant to the new experimental results. E. A. M.-H.

6. SURFACE CHEMISTRY AND COLLOIDS.

The vast range of these two subjects has rendered it impossible to touch on more than a fraction of the work being published; instead of attempting to cover much ground, two restricted fields have been selected for this year's Report, and an attempt made to present a readable account of the more important advances during the last few years in these fields. The reporter is only too well aware that even in these fields much has been deliberately, and perhaps much more inadvertently, omitted.

Colloidal Electrolytes with Long Hydrocarbon Chains.

Great advances have been made during recent years in our knowledge of aqueous solutions of substances containing, at the end of a long hydrocarbon chain, a water-soluble and electrolytically dissociated group. Besides the soaps, this class of substance includes many with strongly dissociated, non-hydrolysable end groups, giving ions such as $R{\cdot}SO_3{}'$, $R{\cdot}O{\cdot}SO_3{}'$, $R{\cdot}NMe_3{}^{\cdot}$. These substances have lately come into great prominence industrially on account of their powerful wetting and detergent action, compounds with many different end groups having been synthesised and patented, and not a few placed on the market. The whole class, including soaps, has recently been called by G. S. Hartley the "paraffin-chain salts," a name perhaps preferable to the alternative "long-chain salts," as the latter would be applicable to numerous classes of highly polymerised compounds containing long chains with oxygen or nitrogen atoms conferring considerable water-attracting power on the chains. The peculiar properties of these substances, which render them so active as depressants of surface or interfacial tension, are due to their unsymmetrical structure, with the very strongly hydrophilic group at one end of a great length of hydrophobic chain.

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[24] B. I. Svešnikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **3**, 61; T. S. Wheeler, *Proc. Indian Acad. Sci.*, 1936, **4**, 291; K. S. G. Doss, *ibid.*, p. 23; E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 1381.

[25] *J.*, 1936, 1014; "Physical Aspects of Organic Chemistry," Routledge, 1935.

F. Krafft's early studies[1] showed that the soaps have such low osmotic activity as to be rightly called colloids in aqueous solution. J. W. McBain's recognition[2] in 1913 that their simultaneous high electrical conductivity and low osmotic activity require the presence of large electrical charges on the "micelles" or colloidal particles was the commencement of his well-known researches with many collaborators[3] on soap solutions, which have established the ionic micelle as perhaps the most characteristic feature of these solutions. In the same year A. Reychler[4] independently concluded that cetanesulphonic acid forms charged aggregates with the paraffin chains in the centre and the sulphonic groups outside, from considerations of the water-attracting power of the different parts of the molecules, and in 1921 N. K. Adam[5] assigned the same structure to the ionic micelle from considerations of the forces which orient molecules of this general constitution at surfaces.

In a series of papers,[6-10a] and one short monograph,[11] G. S. Hartley and others have established beyond doubt that the ionic micelle is formed from the paraffin-chain ions, at dilutions much greater than those formerly associated with the ionic micelle, and that its formation is fairly sudden, as the concentration increases, and is accompanied by (*a*) a marked *decrease* (not an increase, as had previously been supposed) in the total equivalent conductivity[12] of the solution, (*b*) an increase in the mobility of the paraffin-chain ions, (*c*) an enormous increase in the solubility of the whole salt in water, and certain other changes. A good deal of light has also been shed on the structure of the ionic micelles, on the way in which the small ions (called the "gegenions") of opposite charge to the paraffin-

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[1] *Ber.*, 1894, **27**, 1747; 1895, **28**, 2566; 1896, **29**, 1328, 1344.

[2] *Trans. Faraday Soc.*, 1913, **9**, 99.

[3] Cf. *J.*, 1919, **115**, 1279; 1922, **121**, 2325; 1923, **123**, 2417; *J. Amer. Chem. Soc.*, 1920, **42**, 426; 1928, **50**, 1636; 1933, **55**, 545, 2250, 2762; 1935, **57**, 1905, 1909, 1913, 1916; *Proc. Roy. Soc.*, 1920, *A*, **97**, 44; 1933, *A*, **139**, 26.

[4] *Kolloid-Z.*, 1913, **12**, 283.

[5] *Proc. Roy. Soc.*, 1921, *A*, **99**, 348.

[6] J. Malsch and G. S. Hartley, *Z. physikal. Chem.*, 1934, *A*, **170**, 321.

[7] R. C. Murray and G. S. Hartley, *Trans. Faraday Soc.*, 1935, **31**, 183.

[8] J. L. Moillet, B. Collie, C. Robinson, and G. S. Hartley, *ibid.*, p. 120.

[9] G. S. Hartley, *ibid.*, p. 31.

[10] G. S. Hartley, B. Collie, and C. S. Samis, *ibid.*, 1936, **32**, 795.

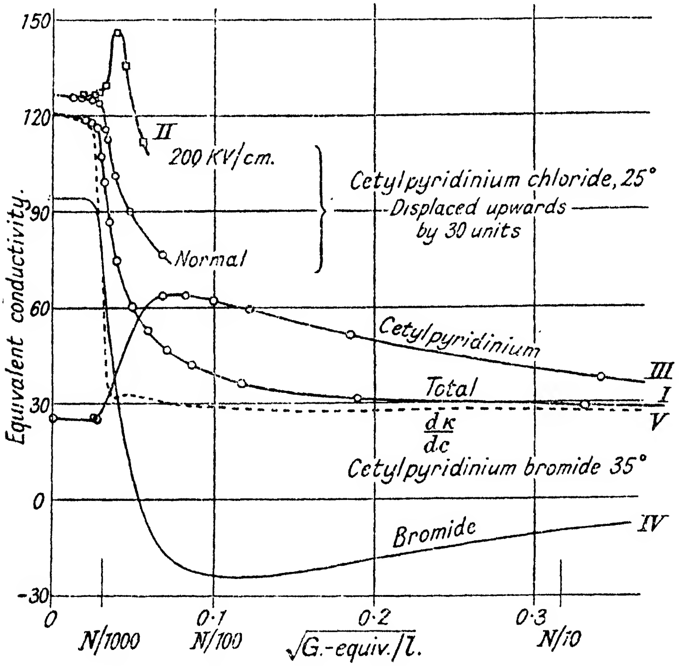
[10a] G. S. Hartley, *J. Amer. Chem. Soc.*, 1935, **58**, 2347.

[11] G. S. Hartley, "Aqueous Solution of Paraffin Chain Salts," Actualités Scientifiques et Industrielles, Paris, 1936.

[12] The expression "total equivalent conductivity" is here used instead of the more usual "equivalent conductivity," to distinguish it from the "equivalent conductivity of the paraffin-chain ions," a term which Hartley has used in place of "mobility" as it is more informative; the last two will be used interchangeably here.

chain ions adhere to the micelles, partially neutralising their charge, and on the solvent properties of the interior of the ionic micelles, which appear to be almost the same as those of liquid paraffins in bulk, and account for the curious solvent properties of solutions of soaps. It has also been shown that there is no need to postulate "neutral micelles" as well as "ionic micelles" to account for the properties of these solutions.

The total equivalent conductivity of a paraffin-chain salt changes with increasing concentration in the manner of curve I of the figure. The curve given is for cetylpyridinium bromide; similar curves were first obtained with all the important details on the alkyl sodium sulphates by A. Lottermoser and F. Püschel;[13] the cetanesulphonates, trimethylcetylammonium salts, and some other paraffin-chain salts with 16 carbon atoms in the chain show closely similar curves.



The main features are: below about $N/1000$, the curve (plotted against the square root of the concentration) is the ordinary linear one of a uni-univalent electrolyte; beyond this concentration (A), the conductivity falls very sharply; with increasing concentration, the fall becomes gradually less steep and finally ceases. At still

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[13] *Kolloid-Z.*, 1933, **63**, 175.

higher concentrations (from $N/20$ to $N/2$ usually), the total equivalent conductivity increases more often than not; in the particular case shown, and in some others, however, there is almost no rise. This rise in the conductivity curves at higher concentrations is always gradual, and is much smaller than the fall commencing at A.

Salts with longer or shorter chains give similar curves, but the concentrations at which the various features, particularly the sudden fall at A, take place are lower the longer the chain;[11, 13, 14] *e.g.*, for a 12-carbon chain A occurs at about $N/100$, instead of $N/1000$ for a 16-carbon chain. The specific nature of the end groups makes minor differences only; the "critical concentration" A is some 30% lower for $\cdot O\cdot SO_3K$ than for $\cdot SO_3K$;[15] it is intermediate for $\cdot NMe_3Br$. Rise of temperature increases the critical concentration somewhat.[13, 14] Bivalent positive gegenions (*e.g.*, in the zinc alkyl sulphates) give a decidedly lower critical concentration than univalent.[13] Addition of ordinary uni-univalent salts to the solution lowers the critical concentration, but little quantitative evidence is available yet on the amount of this lowering.

With solutions of soaps, hydrolysis of the end groups complicates matters in very dilute solutions, so that the curve rises above the linear one for uni-univalent salts at dilutions considerably below the critical. The most careful measurements show the presence of the discontinuity at A, however.[16]

G. S. Hartley brings ample evidence that the discontinuity at A is associated with the start of aggregation of the paraffin-chain ions into ionic micelles. There are three main consequences of this aggregation: (1) a diminished viscous resistance to flow of a given number of these ions through the water, by Stokes's law, as McBain pointed out in 1913; (2) a much increased "braking" effect of the Debye–Hückel atmospheres of oppositely charged gegenions, and (3) a considerable diminution of the total charge on the aggregated ions through the adherence of gegenions sufficiently closely to travel with the micelles, in the opposite direction to that which they would take if free. Under ordinary conditions, (2) and (3) predominate over (1), so the equivalent conductivity falls when micelles are formed.

If, however, the conductivity is measured at extremely high field strengths, as in curve II (200 kV./cm.), the conductivity rises instead of falling at A.[6] M. Wien has shown that at these high field strengths the effects of ionic atmospheres are very much reduced,

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[14] O. R. Howell and H. G. B. Robinson, *Proc. Roy. Soc.*, 1936, *A*, **155**, 386.

[15] G. S. Hartley, *op. cit.*, p. 36.

[16] P. K. Ekwall, *Acta Acad. Åboensis* (*Math. Phys.*), 1927, **4**, 46; *Z. physikal. Chem.*, 1932, *A*, **161**, 195.

because the ions move so rapidly that the atmospheres have not time to form properly.[17] This diminishes (2); and owing to the diminished concentration of gegenions near the micelle, the equilibrium between adherent and free gegenions is probably so altered that many of the adherent gegenions leave the micelle, so that effect (3) is also much diminished. Consequently the effect (1), the diminution of resistance to motion resulting from aggregation, now predominates, and the conductivity rises at the concentration where micelles begin to form. The later fall of the curve is due to the much increased stability of the ionic atmospheres as the concentration increases, so that the effects (2) and (3) again predominate, even under the maximum field strength attainable short of actual sparking.

The total equivalent conductivity, including effects due to the gegenions equally with those due to the paraffin-chain ions, is not the best quantity to employ for detecting changes in aggregation of the latter. Curve III shows the mobility, or equivalent conductivity, of the paraffin-chain ions, obtained as usual from measurements of conductivity and transport number; the latter were measured by an interesting new method, the " balanced boundary " method.[18] In all cases yet examined [10, 11] the mobility of the paraffin-chain ions increases suddenly at the critical concentration. At the same time, the mobility of the gegenions decreases even more markedly than the total equivalent conductivity, and soon becomes negative. The change of sign of the mobility of the gegenions can only mean that a large proportion of them adhere to the paraffin-chain micelles and travel with them in the opposite direction to that which they would take if free.

The effects due to the ionic atmospheres have been estimated, but only semi-quantitatively,[9, 10] on account of the difficulties which the Debye–Hückel theory presents when applied to ions of the very high valency of the micelles. The braking effect is certainly much greater than would be found with uni- or bi-valent ions. Whether or not there is any sharp distinction between the gegenions in the atmospheres and those adhering sufficiently closely to move with the micelles is not certain, so perhaps the effects (2) and (3) above are not sharply distinguishable; but that adherence occurs and that the effective charge on the micelles and their current-carrying capacity are very much diminished is beyond doubt, on account of the transport-number measurements.

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[17] J. Malsch and M. Wien, *Ann. Physik*, 1927, **83**, 305; M. Wien, *ibid.*, p. 327; 1928, **85**, 795; 1929, **1**, 400; *Physikal. Z.*, 1927, **28**, 834; 1929, **30**, 196; cf. G. Joos, *Physikal. Z.*, 1928, **29**, 755; M. Blumentritt, *Ann. Physik*, 1928, **85**, 812.

[18] G. S. Hartley, B. Collie, and E. Drew, *Trans. Faraday Soc.*, 1934, **30**, 648.

The number of paraffin-chain ions and gegenions which go to make up an ionic micelle can only be provisionally estimated at present. The most probable *size* of the micelle, *i.e.*, the number of paraffin-chain ions, may be estimated from considerations of the dimensions of the single ions.[10, 11] A 16-carbon chain is about 18 A. long; 3 A. being added for the end group, the length of the whole ion is about 21 A. The attraction between the end groups and water is so much greater than that between the latter and the chains that it is very unlikely the micelles will contain hydrophilic end groups in their interior; the largest micelles of 16-carbon-chain ions must be 42 A. in diameter, if a sphere; this implies about 50 paraffin-chain ions. If the micelles are not spherical, but elongated, they may be longer than this when they have reached their maximum size, and contain more paraffin-chain ions. G. S. Hartley has calculated that the surface energy of the various parts of these ions is more than sufficient to bring this number together against the repulsive electrostatic forces which arise from bringing together the charged end groups on the surface of the micelles.

The number of adherent gegenions could be found from the mobilities, if the effects of the Debye–Hückel atmospheres could be exactly calculated; an approximate estimate [10] gives, for the fraction of the gegenions adhering, in the dilute solutions in which they are first formed, about 0·74; this gives as the net charge on a micelle of 50 paraffin-chain ions, about 13 units, no fewer than about 37 gegenions being dragged along with the micelle.

McBain and others [19] had observed some of the curious changes in transport number with increasing concentration, and concluded from these and other observations that there is present, in addition to the ionic micelle, neutral colloid. Their theory involved, originally, the presence of a certain proportion of uncharged colloid and ionic micelle carrying the full number of charges associated with the number of single paraffin-chain ions in the micelle. It was, unfortunately, worked out without full consideration of the ionic atmospheres; and many diagrams of the constitution of soap solutions with the proportions of uncharged colloid and entirely un-neutralised ionic micelle required by this theory have appeared.[20] G. S. Hartley [10, 21] has shown that these diagrams can be replaced by much simpler ones, in which there is no " neutral colloid," but the ionic micelle is partially neutralised by the adherent gegenions, whose number varies somewhat with variation in concentration of the solutions. This appears far more probable than that two sharply

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[19] Cf. particularly J. W. McBain and R. C. Bowden, *J.*, 1923, **123**, 2417; McBain, *J. Amer. Chem. Soc.*, 1928, **50**, 1636.

[20] Cf. " International Critical Tables," 1929, **5**, 448.

[21] *Op. cit.*, p. 56.

distinguished types of colloidal micelle exist simultaneously, one uncharged and the other bearing the full charge of all its paraffin-chain ions.

The suddenness of the discontinuity at the critical concentration for micelle formation indicates that the proportion of micelles increases very rapidly as the concentration increases; this is even more striking if the "differential equivalent conductivity" $d\kappa/dc$, or $\lambda + c\,.\,d\lambda/dc$, where κ is the specific and λ the equivalent conductivity, is plotted against concentration (curve V). Consideration of the mass-action equilibrium between the single ions and micelles containing a large number of single ions shows that there is reason to expect [7, 22] a very sudden change from infinitesimal micelle concentration to a solution consisting almost entirely of micelles, if as many as 50 ions unite to form one micelle. If there were an infinite number of single ions in the micelles, the change would be entirely abrupt, as with any other phase change. G. S. Hartley considers that the discontinuity is not quite so abrupt as if nothing but 50-ion micelles were formed from the start, and suggests that a proportion of smaller micelles, containing perhaps about 10 ions, is formed at first. When the concentration has reached from two to five times the critical, it is thought that practically the whole of the salt is in the form of ionic micelles, with about 50 ions.

Fairly sudden changes in other properties of the solution, besides those associated with the transport of electricity, would be expected when micelle formation commences. Perhaps the most remarkable of these is in the solubility of the paraffin-chain salts, which changes with temperature in a characteristic and very unusual manner. Below a certain temperature, which depends both on the length of the chains and on the nature of the end group, the solubility increases with temperature in a normal manner. Above this temperature, the solubility increases extremely rapidly, so much so that only 5° or 7° above a temperature at which the solubility is but a small fraction of 1%, the paraffin-chain salt may be almost indefinitely soluble, solutions of 50% and upwards being easily obtainable. This is explained by the ionic micelle's being extremely soluble, whereas the single ions are but slightly soluble; as the temperature rises, the solution becomes gradually richer in single ions, until a critical concentration is reached at which the equilibrium shifts quickly over to the side of ionic micelles, so that there is no impediment to very high solubilities. G. S. Hartley and R. C. Murray [7] show theoretically that the rate of increase of solubility with temperature should be rather less abrupt than the actual transition between single ions and micelles.

[22] *Op. cit.*, pp. 23 ff.

C. R. Bury has found appreciable changes in the density and the partial specific volume of paraffin-chain salts as the critical concentration is passed;[23] this work includes observations on the octoates and the laurates. Some tendency to micelle formation is found even in butyric acid solutions.[24]

Another effect of ionic micelle formation is a displacing effect on the equilibrium point of various acidimetric indicators.[25] If paraffin-chain salts are gradually added to buffered solutions containing indicators, there is little colour change until the concentration is sufficient for micelles to form, whereupon it may change by as much as corresponds to 1 or 2 units of p_H. The sign of the charges on the ionic micelle and the indicator ions determines whether or not the equilibrium is displaced; and G. S. Hartley has given rules for the choice of indicators not subject to displacement from this cause, which leads to considerable errors in p_H determination by colorimetric methods.

The activity and osmotic coefficients of the solutions are very much lowered, naturally, by micelle formation.[26] The aggregation reduces the osmotic activity of the paraffin-chain ion to practically nil; and that of the gegenions must also be lowered very considerably by the Debye–Hückel effect and the adherence of gegenions to the micelles.[27] J. W. McBain and M. D. Betz[28] have demonstrated the very great decrease in the activity of the hydrogen ion in solutions of various paraffin-chain sulphonic acids, as the concentration rises above the critical; but it should be mentioned that here the sharp discontinuity at the critical concentration has been missed. No one appears as yet to have obtained sufficiently accurate osmotic measurements in dilute solution to detect the discontinuity due to incipient micelle formation, except perhaps with potassium octoate.[29]

It remains to account for the changes in conductivity and mobility at concentrations above those at which the formation of the ionic micelle is complete, according to the theory given above. With the 16-carbon chains, the total equivalent conductivity may rise a little above $N/20$; this rise was, at one stage of McBain's theories, attributed to ionic micelle formation in addition to a large amount of neutral colloid. The mobility of the paraffin-chain

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[23] D. G. Davies and C. R. Bury, *J.*, 1930, 2263; C. R. Bury and G. A. Parry, *J.*, 1935, 626.

[24] J. Grindley and C. R. Bury, *J.*, 1929, 679.

[25] G. S. Hartley, *Trans. Faraday Soc.*, 1934, **30**, 444.

[26] Cf. McBain *et al.*, ref. (3).

[27] G. S. Hartley, B. Collie, and C. S. Samis, ref. (10), p. 812.

[28] *J. Amer. Chem. Soc.*, 1935, **57**, 1913.

[29] J. W. McBain, M. E. Laing, and A. F. Titley, *J.*, 1919, **115**, 1291.

ions begins to decrease (see figure) at about $0{\cdot}005N$, and simultaneously that of the gegenions begins to increase, and these changes go on steadily up to above $N/10$. Increase of concentration would be expected, if no other changes occurred in the solution, to *decrease* the mobility of all the charged particles, owing to the increased braking effects of the ionic atmospheres. The observed increase in mobility or equivalent conductivity of the gegenions indicates that some of the adherent gegenions come off the micelles as they become more crowded in the solution. Although conditions in such concentrated solutions are so complex that exact calculation seems impossible, some effect of this kind seems very probable. At $N/10$, the micelles occupy some 3% of the total volume, so that close approach must occur frequently; and when this takes place, the charges on the surface of one micelle will tend to pull off the gegenions adhering to the other.

Soap solutions have, in addition to their emulsifying power, considerable solvent power for organic compounds insoluble, or very slightly soluble, in water. S. U. Pickering [30] and E. Lester Smith [31] have called attention to this, which indeed can scarcely be overlooked by anyone conducting organic preparations in the course of which any quantity of soap is formed. G. S. Hartley makes the most interesting suggestion [32] that this solvent property is due to the solute's going into the interior of the ionic micelles, which is almost precisely similar to a liquid paraffin in nature. It has been shown that the amount of azobenzene which will go into a solution of a paraffin-chain salt consisting mainly of micelles is proportional to the amount of the salt present. As this substance, and many others which dissolve similarly in solutions containing ionic micelles, are very soluble in liquid paraffins, but insoluble or very slightly soluble in water, and also do not form solid solutions with paraffins, it is concluded that the interior of the ionic micelles is a chaotic arrangement of hydrocarbon chains possessing all the properties of a liquid.

The very pronounced elastic properties of many paraffin-chain salt solutions are ascribed by Hartley,[33] following a suggestion of A. S. C. Lawrence,[34] to adhesion between micelles; as this adhesion is by the exterior of the micelles, the nature of the end groups is of great importance. Adhesion such as this may perhaps have something to do with the explanation of the results of ultrafiltration

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[30] *J.*, 1917, **111**, 86.

[31] *J. Physical Chem.*, 1932, **36**, 1401, 1672.

[32] *Op. cit.*, pp. 41 ff.

[33] *Ibid.*, pp. 58 ff.

[34] *Trans. Faraday Soc.*, 1935, **31**, 189.

measurements of soap solutions carried out by J. W. McBain and others.[35]

Recent Work on Unimolecular Films.

The structure of the "liquid-expanded" type of unimolecular film of long-chain fatty substances on water has been explained at last by I. Langmuir,[36] who uses the very bold conception that the upper, hydrocarbon parts of the molecules adhering to the water by their lower, soluble, end groups form a liquid layer with sufficient of the properties of a phase in bulk to have both an upper and a lower surface tension; the upper surface is supposed to have the same tension as that of a paraffin in bulk; the lower is similar to an interface between a paraffin oil and water, containing a few fatty-acid molecules in addition to the paraffin. Such films form, according to Langmuir, the limiting case of an oil caused to spread on water through the presence of water-attracting groups in the water–oil interface. These films had proved exceedingly difficult of interpretation; the work of N. K. Adam and G. Jessop,[37] in particular, having shown that they have an area and a compressibility intermediate between that of the condensed films, in which the molecules stand nearly upright and are closely packed, and that of molecules lying flat. It was obvious that there was some considerable degree of tilt in the molecules; it was supposed that the thermal agitation produced a state of chaotic agitation in the hydrocarbon chains, but there seemed no reason why the film should cohere, instead of spreading to unlimited areas, like the "gaseous" type of film, or why the area should so often be about 2½ times that of the molecules standing upright. Langmuir points out that the relation between the outward spreading force or "surface pressure" of these liquid-expanded films is identical with the spreading force of a thin layer of a hydrocarbon oil on water, when a certain number of fatty acid molecules are present in the interface between the oil and the water. The theory appears to meet all the facts, and provides an explanation for the failure to spread indefinitely in the cohesion of the "liquid" layer formed by the hydrocarbon portions of the molecules, a liquid layer only some four-fifths of a molecule thick! If a layer of this thickness only can possess the properties of a liquid, there can be no objection to the interior of the ionic micelle possessing them also, as suggested at the end of the preceding section.

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[35] J. W. McBain and W. J. Jenkins, *J.*, 1922, **121**, 2325; J. W. McBain, Y. Kawakami, and H. P. Lucas, *J. Amer. Chem. Soc.*, 1933, **55**, 2762.

[36] *J. Chem. Physics*, 1933, **1**, 756; cf. also 3rd Colloid Symposium Monograph, 1925, 71; Alexander, "Colloid Chemistry," 1926, vol. 1, 525.

[37] *Proc. Roy. Soc.*, 1926, *A*, **112**, 362; cf. also N. K. Adam, W. A. Berry, and H. A. Turner, *ibid.*, 1928, **117**, 532; N. K. Adam, *ibid.*, 1930, **126**, 366.

The transition between liquid-expanded and condensed films presents some curious features, resembling in some ways, but not exactly, a phase change in the surface; Langmuir considers that it indicates a condensation of the molecules into surface " micelles " of from five to thirteen single molecules—the numbers cannot be estimated with great accuracy, though they are probably not the same for all different types of end group in the molecules—and that these micelles have a constant surface vapour pressure, but themselves behave as the units in a " gaseous " type of film. This part of the theory is more difficult to test experimentally than that dealing with the expanded films alone, but appears to fit the surface-pressure measurements.

The transition region between the expanded and the condensed films appears, however, from measurements of the surface potential taken at different parts of the surface, to consist often of at least two types of film in patches large enough to give a fluctuating potential as the exploring air electrode moves over the surface. It will be remembered that the surface potential, or the change in contact potential between the water and the air caused by the presence of a unimolecular film at the surface, is measured with a metallic wire just above the water, the end of the wire being coated with a little radioactive material to render the air conducting.[38]

A film consisting of patches appears inhomogeneous to a moving air electrode. J. H. Schulman and A. H. Hughes [39] found small fluctuations with films of myristic acid, and N. K. Adam and J. B. Harding [40] found fairly large ones with margaronitrile, in the transition region. Such patches must be of the order of millimetres across, as the air electrode is usually about 1 mm. above the surface, and can scarcely be accounted for by micelles consisting of a few molecules only. The transition region appears to require further investigation, in order to account for this patchy structure. Apart from this obscure point, the structure of unimolecular surface films of long-chain fatty substances on water now appears to be fairly well understood.

A beginning has been made with the investigation, by F. A. Askew and J. F. Danielli,[41] by methods analogous to those used for insoluble films at water–air surfaces, of films at the interface between an aqueous and a non-aqueous, immiscible, liquid. Preliminary

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[38] Cf. J. Guyot, *Ann. Physique*, 1924, **10**, 506; A. Frumkin, *Z. physikal. Chem.*, 1925, **116**, 486; J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.*, 1931, *A*, **130**, 259; N. K. Adam and J. B. Harding, *ibid.*, 1932, **138**, 411; *Trans. Faraday Soc.*, 1933, **29**, 837.

[39] *Proc. Roy. Soc.*, 1932, *A*, **138**, 443.

[40] *Ibid.*, 1933, *A*, **143**, 107.

[41] *Ibid.*, 1936, *A*, **155**, 695.

results at the interface between bromobenzene and water indicate that, for long-chain aliphatic compounds, the lateral adhesion in the films, due to hydrocarbon chains, is much less when these are immersed in a non-polar or slightly polar liquid than at the water–air interface. This is because the chains are moved about among the molecules of the liquid; their surface energy does not have to be satisfied, as in the case of a water–air surface, by close adhesion to the hydrocarbon chains of other molecules in the film, but is satisfied by adhesion to the molecules of the non-aqueous liquid, which are in constant translatory motion.

As a general rule, mere presence at a *liquid* surface does not appear to alter the intrinsic reactivity or energy of activation of a molecule. In this respect liquid surfaces differ, of course, from solid. Nevertheless, it has been shown that the rate of reaction of a substance at a liquid surface may be influenced by the special conditions prevailing at the surface, through change in the accessibility of the reacting groups in the molecules at the surface to reagents in the substrate or underlying liquid. A striking instance of this was found by A. H. Hughes and E. K. Rideal[42] in the oxidation of acids containing a double bond in the middle of the hydrocarbon chain, such as oleic or petroselinic acid, by permanganate in the underlying water. The rate of oxidation is nearly ten times as great when the film is under low compression, so that the molecules frequently lie nearly flat, as when the film is highly compressed and the double bonds in the molecules have less chance of reaching the water. These films are of the expanded type, *i.e.*, the molecules are oscillating in a chaotic manner, so that probably all parts of the hydrocarbon chain come into contact with the water at one time or another; but the chance of the upper and middle parts of the chains reaching the water is much greater if the film is not too highly compressed. Similar results have been obtained on the more highly unsaturated addition compound of elæostearin and maleic anhydride by G. Gee and E. K. Rideal;[43] A. H. Hughes[44] finds that snake venoms in the substrate hydrolyse the oleyl chains off lecithin in a unimolecular film on the surface more easily if the lecithin film is not highly compressed; *i.e.*, if the double bonds in the oleyl chains can easily reach the water.

In all such work, as indeed in all work on surface films, there is a risk of changes in the surface being due, not to actual chemical changes in the substance originally spread in the film, but to the arrival, often accidental, of other substances at the surface from the

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[42] *Proc. Roy. Soc.*, 1933, *A*, **140**, 233; cf. also A. H. Hughes, *J.*, 1933, 338.

[43] *Proc. Roy. Soc.*, 1935, *A*, **153**, 116.

[44] *Biochem. J.*, 1935, **29**, 437.

solution. In this connexion the very slow rates of adsorption of dilute solutions of certain paraffin-chain salts may be of interest: N. K. Adam and H. L. Shute,[45] also R. C. Brown[46] by a different method, found that the final surface tension in extremely dilute solutions may not be reached for days. A curious fact is that, if the concentration is high enough for ionic micelles to be present, the final tension is reached almost at once. Incidentally, R. C. Brown finds that the "ripple" method for determining surface tension gives values as low as the usual static methods, proving that when ripples pass over the surface of an aqueous solution there is no displacement of the solute from the surface. It has been shown by J. H. Schulman and A. H. Hughes[47] that some soluble but strongly surface-active substances, especially soaps and other paraffin-chain salts, will displace such substances as tripalmitin from a unimolecular film on the surface, by reason of their own tendency to pass from the interior of the solution to its surface. Protein films also may be displaced.

Besides the long-chain fatty substances, the sterols,[48] and many allied complex ring structures,[49, 50, 51] form very stable unimolecular films, which have been investigated for several years by N. K. Adam, F. A. Askew, J. F. Danielli, and others. Very frequently the principal or the only water-soluble group is found at the extreme end of the molecule, any aliphatic side chain, if present, being at the opposite end; and usually surface films of such substances have the molecules standing upright in the surface, closely packed and forming very coherent films. Exceptions do, however, occur, the most notable being with coprostenone, the ketone formed by oxidation of the sterol cholesterol. The change of the CH(OH) group into CO, without any change of position, results in the molecules becoming very much tilted to the vertical, and the area increasing by nearly 50%. Some other substances, particularly ketonic derivatives of

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[45] *Trans. Faraday Soc.*, 1935, **31**, 204.

[46] *Ibid.*, p. 205; *Proc. Physical Soc.*, 1936, **48**, 312.

[47] *Biochem. J.*, 1935, **29**, 1236, 1243.

[48] Sterols: N. K. Adam, *Proc. Roy. Soc.*, 1928, *A*, **120**, 473; N. K. Adam and O. Rosenheim, *ibid.*, 1929, *A*, **126**, 25; 1929, *B*, **105**, 422; J. F. Danielli and N. K. Adam, *Biochem. J.*, 1934, **28**, 1583; N. K. Adam, F. A. Askew, and J. F. Danielli, *ibid.*, 1935, **29**, 1786.

[49] Oestrin derivatives: N. K. Adam, J. F. Danielli, G. A. D. Haslewood, and G. F. Marrian, *ibid.*, 1932, **26**, 1233; Danielli, Marrian, and Haslewood, *ibid.*, 1933, **27**, 311.

[50] Sapogenins: F. A. Askew, S. N. Farmer, and G. A. R. Kon, *J.*, 1936, 1399.

[51] Resinols: F. A. Askew, *ibid.*, p. 1595; W. D. Harkins, H. E. Ries, and E. F. Carman, *J. Amer. Chem. Soc.*, 1935, **57**, 2224; 1936, **58**, 1377; *J. Chem. Physics*, 1936, **4**, 228.

sterols, show the same effect in lesser degree. Irradiation of ergosterol produces the same effect. The cause remains a complete mystery, and the fact, with the possibility of tilt of the molecules occurring even when there is only one water-soluble group at the extreme end of the molecule, renders it much more difficult to make deductions as to the constitution of new members of this class of compound from surface-film measurements than had been hoped. The oestrin group has proved interesting, in so far as derivatives of the same parent substance, differing only in the number and position of certain water-soluble groups, stand on one or the other end of the ring system, in the surface films; and may also, with appropriate distribution of water-soluble groups, lie flat in the surface. These results are quite simply interpreted in the light of the constitution of the molecules.[49]

The surface-film measurements give a measurement of the size of organic molecules in certain packings and orientations on the water surfaces, and have been used as an aid in determining the constitution of various substances; the size and properties of the surface films to be expected for a given constitution can often be foretold from measurements on nearly related compounds, or even on models of the molecules. It was shown by B. C. J. G. Knight,[52] for instance, that batyl alcohol, known to be an ether of glycerol with one molecule of octadecyl alcohol, has the long chain on one of the terminal hydroxyls in the glycerol, not on the centre one, by a comparison of surface films of this substance with those of α-monopalmitin; the films are very closely similar, but quite different from those to be expected if the long chain were attached to the central hydroxyl group. This conclusion, disputed at first, was afterwards confirmed by more ordinary methods.[53] Surface-film measurements on the sterols are quite inconsistent with the older formulæ, but consistent with the new and now universally adopted formulæ of O. Rosenheim and H. King.

Cellulose derivatives,[54] proteins,[55, 56] and highly polymerised synthetic substances containing numerous hydroxyl groups in the

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[52] *Biochem. J.*, 1930, **24**, 257; cf. N. K. Adam, *J.*, 1933, 164.

[53] W. H. Davies, I. M. Heilbron, and W. E. Jones, *J.*, 1933, 165; 1934, 1232.

[54] N. K. Adam, *Trans. Faraday Soc.*, 1933, **29**, 90; N. K. Adam and J. B. Harding, *ibid.*, p. 837.

[55] E. Gorter and others, *Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 371; 1926, **29**, 1262; 1929, **32**, 770; 1932, **35**, 838; 1933, **36**, 922; 1934, **37**, 20, 355, 788; *J. Gen. Physiol.*, 1935, **18**, 421; *Biochem. J.*, 1935, **29**, 38, 48.

[56] A. H. Hughes and E. K. Rideal, *Proc. Roy. Soc.*, 1932, *A*, **137**, 62; A. H. Hughes, *Trans. Faraday Soc.*, 1933, **29**, 214; J. H. Schulman and A. H. Hughes, *Biochem. J.*, 1935, **29**, 1236.

chains [57] generally lie flat in the surface, if they can be spread at all. Complete spreading is decidedly difficult to obtain, and practically no spreading is obtained if the protein is first denatured.[58] When spread, the protein films, and the cellulose films, may be compressed or expanded somewhat without collapsing; in the case of the protein films this is considered by A. H. Hughes and E. K. Rideal to be a folding of the chains without leaving the surface, similar to those caused by stretching protein fibres. N. K. Adam [54] considers that the compressibility of cellulose derivatives is due to a tilt of the unit glucose rings slightly away from the surface on lateral compression.

Finally, some interesting work on the transference of oriented films of long-chain molecules from water surfaces to solids must be mentioned.[59] By repeatedly dipping a clean glass, or polished metal, plate into water covered by unimolecular films, layers may be deposited one by one. Generally, the first layer has the polar groups oriented towards the glass or metal, the next has them outwards, and so on alternately. The structure is very similar to that of crystals of these paraffin-chain compounds. If the outer layer has the hydrocarbon ends of the molecules outwards, the surface is not easily wetted by water; but if it has the water-attracting groups outwards, it is perfectly wetted. In certain circumstances successive layers can be deposited all with the hydrocarbon chains pointing outwards.

Even one of these layers, as I. Langmuir showed in 1920,[60] has a considerable lubricating effect on the solid.

N. K. A.

7. The Effect of the Solvent in the Measurement of Dipole Moments.

Although it was realised before 1932 that, when determined in solution, the dielectric polarisation of a compound possessing a resultant dipole moment varied somewhat with the nature of the solvent, even when the results were extrapolated to infinite dilution, it was generally believed that the differences were not considerable and that the dipole moments calculated from data obtained in this manner

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[57] W. D. Harkins, E. F. Carman, and H. E. Ries, *J. Chem. Physics*, 1935, **3**, 692.

[58] H. Neurath, *J. Physical Chem.*, 1936, **40**, 361.

[59] K. B. Blodgett, *J. Amer. Chem. Soc.*, 1934, **56**, 495; 1935, **57**, 1007; I. Langmuir and V. J. Schaefer, *ibid.*, 1936, **58**, 284; G. L. Clark, R. R. Sterrett, and P. W. Leppla, *ibid.*, 1935, **57**, 330.

[60] *Trans. Faraday Soc.*, 1920, **15**, 68.

were in good agreement with those derived from measurements on the vapour. The results of F. H. Müller[1] on the polarisation of chlorobenzene in a number of solvents called attention, however, to the possibility that the solvent influence might be appreciable, and that dipole moments estimated from measurements in dilute solution might require reconsideration. In the past three years many studies of the solvent influence on dielectric polarisation have been made, from both theoretical and experimental points of view, and Müller's results have been substantiated and extended. One of the objects of this work has been to discover a relationship between the moment determined in solution and the true value, it being assumed that the latter is given by the vapour–temperature method based on the well-known Mosotti–Clausius–Debye equation. The treatment may be divided very roughly into three sections: (*a*) empirical methods for correcting for the solvent influence, (*b*) theoretical consideration of factors not included in the Debye equation, (*c*) fundamental modifications of this equation. It will be assumed, for the present, that the deviation from ideal behaviour is to be ascribed to electrical interaction between solvent and solute, and that no chemical action occurs.

(a) *Empirical Corrections for the Solvent Influence.*—In order to account for the results with a number of substances, F. H. Müller[2] proposed the relationship

$$\frac{({}_{\infty}P_2 - R)_{\text{solution}}}{(P_2 - R)_{\text{vapour}}} = 1 - 0{\cdot}075(\varepsilon - 1)^2 \quad . \quad . \quad . \quad (1)$$

where P_2 and R represent the total polarisation and molecular refractivity respectively of the solute and ε is the dielectric constant of the solvent. The value of ${}_{\infty}P_2$ in solution is obtained by extrapolation to infinite dilution. If the atom polarisation is negligible, then equation (1) can be written, to a first approximation, in the form

$$\frac{\mu_{\text{sol.}}}{\mu_{\text{vap.}}} = 1 - 0{\cdot}038\,(\varepsilon - 1)^2 \quad . \quad . \quad . \quad . \quad (2)$$

This equation implies that the dipole moment measured in solution is *less* than the vapour value, the discrepancy increasing with increasing dielectric constant of the solvent. To obtain the true moment it is necessary to extrapolate the results in solution to the value for a medium of dielectric constant unity. The facts were explained qualitatively by supposing that the intense electrical field of a dipole molecule produced saturation of the dielectric in its vicinity, so that

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[1] *Physikal. Z.*, 1932, **33**, 732.

[2] *Ibid.*, 1933, **34**, 689; *Trans. Faraday Soc.*, 1934, **30**, 729.

the polarisability of the non-polar solvent is decreased below its value in the pure state. The decrease in polarisation of the solution, which is evident as an apparent decrease of moment of the solute, is, according to Müller, due to the solvent. By adapting the method employed[3] for the interpretation of dielectric phenomena in electrolytic solutions, an expression was deduced for the expected change in polarisation of the solvent. It has been pointed out,[4] however, that the almost exact additivity of refractivities in solution argues against the postulate of dielectric saturation. The empirical equation (1) is satisfactory for calculating $\mu_{\text{vap.}}$ in certain instances, but it fails in others,[5] and in any case it can only have limited applicability, since it is now evident that, although for the majority of compounds the apparent dipole moment decreases with increasing dielectric constant of the solvent, yet for some substances, *e.g.*, alcohols, the moment is almost independent of the medium, whereas for others, *e.g.*, chloroform, the moment in solution is greater than that of the vapour.[6]

H. O. Jenkins[7] suggested that $_{\infty}P_2$ in various media is a linear function of $1/\varepsilon$, thus

$$_{\infty}P_2 = A \pm B/\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A and B are constants. By altering the sign in front of the B/ε term, equation (3) could be used to represent both positive and negative solvent effects. This empirical relationship has the advantage of covering a wider range of dielectric constants than equation (1) and appears to be applicable to nitrobenzene, chlorobenzene, and *p*-nitroaniline in a number of solvents, both polar and non-polar. It fails, however, in certain instances to give the correct value for the polarisation when the results are extrapolated to $\varepsilon = 1$. In its simplest form the relationship proposed by S. Sugden,[8] that P_2 is a linear function of the volume polarisation, may be written

$$P_2 = A \pm B(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad (4)$$

so that it covers both types of solvent influence: as will be seen shortly, an equation of this type has a theoretical basis. It has been found to be of the correct form to represent the variation of polarisation with dielectric constant of the medium for a number of dipolar solutes, but it is doubtful if the significance originally attached to A,

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[3] H. Sack, *Physikal. Z.*, 1927, **28**, 199.

[4] F. C. Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171 (172).

[5] C. P. Smyth *et al.*, *J. Chem. Physics*, 1935, **3**, 55, 347, 557; E. G. Cowley and J. R. Partington, *J.*, 1936, 1184; 1937, 130.

[6] K. Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167.

[7] *Nature*, 1934, **133**, 106; *J.*, 1934, 480.

[8] *Nature*, 1934, **133**, 415; *Trans. Faraday Soc.*, 1934, **30**, 720.

as the sum of $P_2^{\text{vap.}}$ and a small constant, and to B, as the orientation polarisation (P_O) of the solute, can be substantiated either theoretically (see below) or from actual measurements. By Sugden's equation the plot of P_2 against $(\varepsilon - 1)/(\varepsilon + 2)$ for various solvents, or for different concentrations in the same solvent, should be a straight line, which on extrapolation to $(\varepsilon - 1)/(\varepsilon + 2) = 0$, that is $\varepsilon = 1$, should give $P_2^{\text{vap.}}$, but this procedure does not always yield satisfactory results.[9] F. Fairbrother [10] has tested equation (4) by plotting P_2 against $(\varepsilon - 1)/(\varepsilon + 2)$ for nitrobenzene in solution at several temperatures, and found, as required, that straight lines converging to a common point for $(\varepsilon - 1)/(\varepsilon + 2) = 1$ are obtained. From the slope of the lines, assumed equal to P_O, the moment was found to be 4·24 D, in excellent agreement with the vapour value. A comprehensive test of equation (4), however, has led H. O. Jenkins and L. E. Sutton [9] to conclude that it is only approximately correct: the value of B is often very different from P_O, and the agreement observed by Fairbrother for nitrobenzene is regarded as fortuitous. Another type of semi-empirical equation is that of R. J. W. Le Fèvre,[11] *viz.*,

$$P'_O/P''_O = K(\varepsilon'' + 2)/(\varepsilon' + 2) \quad . \quad . \quad . \quad . \quad (5)$$

where P'_O and P''_O represent the orientation polarisations for a given solute in two media of dielectric constant ε' and ε'', respectively, and K is a constant approximately equal to unity for a number of substances. If one of the solvents is regarded as a vacuum ($\varepsilon'' = 1$), then it follows that

$$P_O^{\text{sol.}}/P_O^{\text{vap.}} = K3/(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad (6)$$

The use of this equation is restricted by the uncertainty in the value of K, and also because it only applies to negative solvent effects, that is, when polarisation decreases with increasing dielectric constant. In spite of their limitations, and the fact that they cannot be used for accurate extrapolation to $\varepsilon = 1$, one or other of the equations given above may be employed for interpolation purposes, for example, when it is required to compare polarisations of different substances under analogous conditions, *e.g.*, in media of the same dielectric constant. For this purpose a function of ε giving a linear relationship against P_2 is to be preferred: the volume polarisation $(\varepsilon - 1)/(\varepsilon + 2)$, or its square, appears to be best for this purpose.[12]

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[9] H. O. Jenkins and L. E. Sutton, *J.*, 1935, 609; E. G. Cowley and J. R. Partington, *locc. cit.*, ref. (5).

[10] *J.*, 1934, 1846.

[11] *J.*, 1935, 773.

[12] D. P. Earp and S. Glasstone, *ibid.*, pp. 1709, 1720.

(b) *Theoretical Consideration of Factors not included in the Debye Equation.*—Soon after the publication of Müller's work on the polarisation of chlorobenzene, an attempt was made by J. Weigle[13] to explain the results theoretically. Two factors not included in the Debye treatment of dipolar molecules were considered, namely, (i) the polarisation of the medium by the dipolar molecules of solute, and (ii) the orientation of optically anisotropic solvent molecules surrounding the dipole. The second of these factors should produce a moment $\Delta\mu'$, acting in the same direction as the primary moment, given by

$$\Delta\mu' = A(\mu^3/a^6)(\alpha' - \alpha'')^2/kT \quad . \quad . \quad . \quad . \quad (7)$$

where A is a numerical constant, μ is the moment of the dipolar molecule, assumed to be spherical, and a is its radius; α' and α'' are the polarisabilities along the two chief axes of the anisotropic solvent molecule, assumed to be an ellipsoid of revolution. Since $\alpha' - \alpha''$ is involved, $\Delta\mu'$ is evidently small, and for most solvents it is probably of the order of 1% of the primary moment. The main influence of the solvent is attributed to the polarisation of its molecules by the dipoles. If the molecules are spherical, Weigle finds the moments induced by the solute in surrounding molecules should cancel one another, so that the resultant effect is zero. For non-spherical solvent molecules, however, the resultant induced moment is generally not zero: its value and *sign* depend on the actual shape of the molecules. Weigle considered only the case of a molecule consisting of a cone terminating at its point in a spherical surface, and found the resultant induced moment $\Delta\mu$, in the direction of the primary moment, to be given by the following equation, in which small terms have been ignored, *viz.*,

$$\Delta\mu = B\mu(\alpha' + 2\alpha'') \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where the magnitude and *sign* of B depend on the shape of the solute molecule and α' and α'' are the polarisabilities of the solvent. This is virtually the form in which Weigle left his deductions, but further consideration shows that it can be written in another way so as to bring out more explicitly the influence of the dielectric constant of the medium. If the difference in α' and α'' is not great, equation (8) reduces to $\Delta\mu = 3B\mu\alpha$, where α represents the mean polarisability of the solvent molecules, and for a non-polar substance this is given by

$$M(\varepsilon - 1)/d(\varepsilon + 2) = 4/3\pi N\alpha \quad . \quad . \quad . \quad . \quad (9)$$

so that

$$\Delta\mu = \mu C(\varepsilon - 1)/(\varepsilon + 2)$$

or

$$\mu_{\text{sol.}}/\mu_{\text{vap.}} = 1 + C(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad (10)$$

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[13] *Helv. Physica Acta*, **1933**, **6**, 68.

where C is a constant, dependent on the shape of the solute molecule. The relationship between this and Sugden's equation (4) is evident. K. Higasi[6] has shown that Weigle's theory predicts a negative solvent effect for molecules elongated along the dipole axis, and a positive effect for molecules having their elongation perpendicular to this axis. The latter type of molecule should have negative Kerr constants, and it was in fact found that with such substances, only a limited number of which are known, the dipole moment in solution is greater than in the vapour.

The calculation of the moment induced in the solvent by the dipolar solute has been extended by F. C. Frank,[14] who has given a very complete discussion of the solvent effect in the measurement of dipole moment, and independently by K. Higasi.[15] Frank makes use of the relationship $I = E(\varepsilon - 1)/4\pi$ for the induced moment per unit volume, where E is the field strength in the given volume element: the field strength at any point in the vicinity of the dipole, assumed to have no finite length, can be readily calculated. In order to obtain the resultant induced moment it is convenient to divide the space round the dipole into elementary shells of uniform field, and each of these is further divided into elementary rings in which the uniform field is uniformly inclined to the dipolar axis. The induced moment is calculated to be

$$\Delta\mu = A\mu(\varepsilon - 1)/\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or

$$\mu_{\text{sol.}}/\mu_{\text{vap.}} = 1 + A\mu(\varepsilon - 1)/\varepsilon \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where A is a quantity determined by the shape of the molecule and the position of the dipole within it: the value of A may be positive or negative and is evaluated by a process of graphical integration. Actual dipolar molecules may be divided roughly into four categories according to their geometry, with characteristic solvent effects. (i) Small molecules with no large group attached, *e.g.*, HCl, H_2O, for which A is about $+ 0{\cdot}1$, so that the solvent effect should be positive. (ii) Molecules with a radical on the dipole axis, *e.g.*, CH_3Cl, $C_6H_5{\cdot}NO_2$, C_6H_5Cl; nearly all the substances considered by F. H. Müller fall into this category. The solvent effect is negative, and Frank's calculations give results in approximate agreement with Müller's rule (equation 2). (iii) Molecules with a single radical not on the dipole axis, *e.g.*, $CH_3{\cdot}OH$; with such substances the effect depends largely on the angle θ representing the polar co-ordinate of the radical with respect to the dipole axis, the position of the dipole being the origin. If θ is less than 55°, $\Delta\mu$ is negative and of appreci-

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[14] *Loc. cit.*, ref. (4), p. 171.

[15] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284.

able magnitude, but if θ is greater than 55° then $\Delta\mu$ tends to become positive although it is only appreciable when θ is about 90°. For alcohols, the solvent effect might be expected to be small. (iv) Molecules with radicals off the dipole axis but possessing axial symmetry, *e.g.*, $CH_3{\cdot}O{\cdot}CH_3$, $(CH_3)_3N$, $(CH_3)_2CO$; the induced moment in the solvent is, as in case (iii), negative or positive according as θ is less or greater than 55°. For dimethyl ether it should be small, for trimethylamine it should be positive, whereas for acetone it should be negative but not large. The anticipations are in general agreement with experimental observations. It is of interest to record that F. H. Müller and P. Mortier,[16] as a result of measurements with a number of compounds, have divided molecules into groups corresponding closely to those proposed by Frank from theoretical considerations: the former authors also emphasise the importance of the position of the dipole in the molecule, which is determined by Frank's angle θ. Since equation (12) may be written

$$\mu_{\text{sol.}}/\mu_{\text{vap.}} = 1 + A\mu_{\text{vap.}} - A\mu_{\text{vap.}}/\varepsilon \quad . \quad . \quad . \quad (13)$$

it follows that the plot of $\mu_{\text{sol.}}$ against $1/\varepsilon$ should be linear, and when extrapolated to $\varepsilon = 1$ the result should give the true moment in the vapour state. As far as the available data are concerned these anticipations are only realised very approximately, the extrapolated value of $\mu_{\text{vap.}}$ being higher than that observed.[17] Although it is apparent that the main solvent effect is to be attributed to induced polarisation in the solvent molecules, other factors, *e.g.*, distortion of the field surrounding the dipole, various forms of interaction between the molecules of solvent and the solute, and orientation of the solvent molecules on account of their anisotropy, must be taken into consideration. It may be noted that since P_0 is proportional to μ^2, equation (13) reduces to one similar to that of Jenkins [equation (3)], if the term involving $1/\varepsilon^2$ is neglected.

The treatment of K. Higasi [15] is based on the relationship $\Delta\mu = \alpha E$, where α is the polarisability of the solvent molecule, as given by equation (9), and E is the field strength. The value of $\Delta\mu$ is calculated as

$$\Delta\mu = \mu A(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad (14)$$

or

$$\mu_{\text{sol.}}/\mu_{\text{vap.}} = 1 + A(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad (15)$$

which is identical in form with that obtainable from Weigle's treatment: this is to be expected, as Higasi's method is a direct extension of that of Weigle. The sign and value of A depend on the shape of the solute molecule, and a number of cases are considered. (I) If

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[16] *Physikal. Z.*, 1935, **36**, 371.

[17] See, however, E. G. Cowley and J. R. Partington, *J.*, 1936, 1184 (1189).

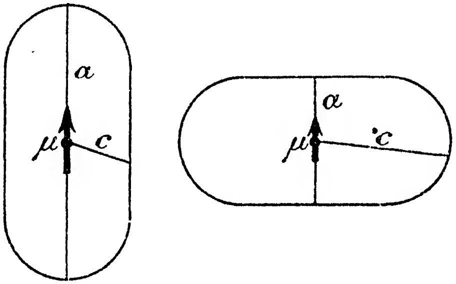
the molecule is spherical, then A is zero and $\mu_{\text{sol.}} = \mu_{\text{vap.}}$. (II) The dipolar molecule has the shape of an ellipsoid of rotation with a dipole at its centre along its axis of symmetry : if a is the radius along the dipolar axis and c the value at right angles, then there are two possibilities, according as (a) $a > c$ (Fig. 1A) or (b) $a < c$ (Fig. 1B). For case (a), the value of A is given by

$$A_{\text{II}a} = \frac{-1}{k^2-1}\left\{1 - \frac{k}{\sqrt{k^2-1}}\log\left(k+\sqrt{k^2-1}\right)\right\} - \tfrac{1}{3} \quad . \quad (16)$$

where k is equal to a/c, the ratio of the radii, which is greater than unity : the value of $A_{\text{II}a}$ is always negative, so that for molecules of this type the solvent effect should always be negative. For case (b) it is calculated that

$$A_{\text{II}b} = \frac{-1}{k^2-1}\left\{1 - \frac{k}{\sqrt{1-k^2}}\sin^{-1}\sqrt{1-k^2}\right\} - \tfrac{1}{3} \quad . \quad (17)$$

where k is now less than unity, and $A_{\text{II}b}$ is always positive, as also is the solvent influence. (III) The solute molecule is an ellipsoid of rotation but the dipole is not at its centre (Fig. 2) : several cases are possible. (a) If $a_1 > c$ and $a_2 > c$, then $A_{\text{III}a}$ is the sum of two terms A_1 and A_2, where



(A) (B)

FIG. 1.

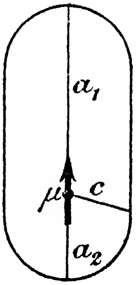


FIG. 2.

$$A_1 = \frac{-c^2}{a_1^2-c^2}\left\{1 - \frac{a_1}{\sqrt{a_1^2-c^2}}\log\frac{a_1+\sqrt{a_1^2-c^2}}{c}\right\} - \tfrac{1}{3} \quad . \quad (18)$$

and A_2 has an analogous value with a_2 replacing a_1 : both A_1 and A_2 are always negative. (b) If $a_1 > c$ and $a_2 < c$, then $A_{\text{III}b}$ is the sum of A_1, as above, and B_2, where

$$B_2 = \frac{-c^2}{a_2^2-c^2}\left\{1 - \frac{a_2}{\sqrt{c^2-a_2^2}}\sin^{-1}\frac{\sqrt{c^2-a_2^2}}{c}\right\} - \tfrac{1}{3} \quad . \quad (19)$$

which is always positive. The actual solvent effect will therefore be either negative or positive according as A_1 is greater or less than B_2. (*c*) If $a_1 < c$ and $a_2 < c$, then

$$A_{\text{III}c} = B_1 + B_2 \qquad \ldots\ldots \qquad (20)$$

where B_2 is as already given and B_1 is the corresponding value when a_1 replaces a_2: both terms are positive. (*d*) If $a_1 < c$ and $a_2 > c$, then

$$A_{\text{III}d} = B_1 + A_2 \qquad \ldots\ldots \qquad (21)$$

which may be negative or positive, according to the relative values of A_2 and B_1. Provided the dipole is not situated far from the centre of the molecule, the results of Higasi may be summarised, in general, by the statement

$$\mu_{\text{sol.}} \gtrless \mu_{\text{vap.}} \text{ according as } a \lesseqgtr c$$

where a and c are measured along the dipolar axis and perpendicular to it, respectively. The main difficulty in the application of the equations given above to determine $\mu_{\text{vap.}}$ from measurements in solution lies in the determination of the shape of the molecule and the position of the dipole in it. This is done approximately from the known atomic dimensions and from stereochemical considerations, the molecule being assumed to be equivalent in shape to an ellipsoid of rotation. Where the necessary data are available, Higasi has shown the calculated values of $\Delta\mu$ to be in good agreement with $\mu_{\text{sol.}} - \mu_{\text{vap.}}$, and the same conclusion has been reached by E. G. Cowley and J. R. Partington,[5] who have made measurements on benzonitrile, propionitrile, bromobenzene, and ethyl bromide in six non-polar solvents. The theory of the electro-optical Kerr effect [18] indicates that positive Kerr constants are, in general, to be expected for molecules in which the dipole lies in the direction of the longer axis, so that they should show negative solvent effects: most compounds have positive Kerr constants, and hence the dipole moments in solution are usually smaller than the vapour values. When the Kerr constant is negative, *e.g.*, for chloroform, the solvent effect is positive: for such substances the dipole is perpendicular to the longer axis of the molecule.[6] Before proceeding, attention may be called to a difference between the equation of Frank and those of Weigle and of Higasi: both the last two involve $(\varepsilon - 1)/(\varepsilon + 2)$, but the first gives $\Delta\mu$ as a function of $(\varepsilon - 1)/\varepsilon$. Since ε for most non-polar solvents is about 2, the general results are not very different, but the discrepancy requires further investigation.

An entirely different approach has been outlined by P. Debye,[19]

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[18] See, *e.g.*, H. A. Stuart, " Molekülstruktur," 1934, p. 197 *et seq.*

[19] *Physikal. Z.*, 1935, **36**, 100; *Chem. Reviews*, 1936, **19**, 171.

based on the theory of quasi-crystalline structure of liquids: the axis of the dipolar molecule is supposed to rotate relatively slowly, so that an additional term is to be added to that of thermal agitation hindering the orientation of dipoles in an external field. The expression for the orientation polarisation per molecule should then be written

$$P_0 = (4\pi\mu^2/9kT) \, . \, F(y) \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where $F(y)$ is a function of $y = E/kT$, E being regarded as the coupling energy between solvent and solute molecules which prevents rapid rotation. The treatment so far has been qualitative; it accounts only for negative solvent effects but does not explain its variation with dielectric constant. It has been suggested that the theory may prove more useful for polar than for non-polar solvents.[4]

(c) *Fundamental Modifications of the Debye Equation.*—Unless a molecule is optically isotropic, *i.e.*, equally polarisable in all directions, neither the Mosotti–Clausius equation nor its extension by Debye to polar molecules can be strictly applicable. (Sir) C. V. Raman and K. S. Krishnan[20] have pointed out that there is much evidence to show that actual molecules are not isotropic; they have considered the general case of a *pure liquid* consisting of anisotropic molecules and have derived the equation

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\left(\Sigma \frac{\alpha}{3} + \frac{\mu^2}{3kT}\right) + \frac{\varepsilon - 1}{\varepsilon + 2} N\left(\Psi + \frac{\Theta}{3kT}\right) \quad . \quad (23)$$

where $\Sigma\alpha = \alpha' + \alpha'' + \alpha'''$, the polarisabilities along three axes, and Ψ and Θ give the effects of anisotropy on the induced and the orientation polarisation, respectively, which can be determined, approximately at least, from measurements of light scattering and from the geometry of the molecule.[21] The equation has been extended to liquid mixtures,[22] then becoming

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M_{1,2}}{d_{1,2}} = f_1\left[\frac{4\pi}{3} N\left(\sum \frac{\alpha_1}{3} + \frac{{\mu_1}^2}{3kT}\right) + \frac{\varepsilon - 1}{\varepsilon + 2} N\left(\Psi_1 + \frac{\Theta_1}{3kT}\right)\right]$$
$$+ f_2\left[\frac{4\pi}{3} N\left(\sum \frac{\alpha_2}{3} + \frac{{\mu_2}^2}{3kT}\right) + \frac{\varepsilon - 1}{\varepsilon + 2} N\left(\Psi_2 + \frac{\Theta_2}{3kT}\right)\right] \quad . \quad (24)$$

where the subscripts 1 and 2 stand for solvent and solute respectively. M. A. Govinda Rau [23] has considered the special case when one of the

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[20] *Proc. Roy. Soc.*, 1928, *A*, **117**, 589.

[21] See (Sir) C. V. Raman and K. S. Krishnan, *Phil. Mag.*, 1928, **5**, 498; K. S. Krishnan and S. R. Rao, *Indian J. Physics*, 1929—30, **4**, 39; M. Ramanadham, *Proc. Indian Acad. Sci.*, 1934, **1**, *A*, 281; H. O. Jenkins and S. H. Bauer, *J. Amer. Chem. Soc.*, 1936, **58**, 2435.

[22] D. S. Subbaramaiya, *Proc. Indian Acad. Sci.*, 1934, **1**, *A*, 355.

[23] *Ibid.*, 1935, **1**, *A*, 498; see also H. O. Jenkins and S. H. Bauer, *loc. cit.*, ref. (21).

components, *i.e.*, the solvent, is non-polar, that is $\mu_1 = 0$ and $\Theta_1 = 0$, so that

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M_{1.2}}{d_{1.2}} = f_1\left[\frac{4\pi}{3} N \sum \frac{\alpha_1}{3} + \frac{\varepsilon - 1}{\varepsilon + 2} N \Psi_1\right]$$
$$+ f_2\left[\frac{4\pi}{3} N\left(\sum \frac{\alpha_2}{3} + \frac{\mu^2}{3kT}\right) + \frac{\varepsilon - 1}{\varepsilon + 2} N\left(\Psi_2 + \frac{\Theta}{3kT}\right)\right] \quad . \quad (25)$$

The molar polarisation of the non-polar solvent in the gaseous state is $\frac{4\pi}{3} N \sum \frac{\alpha_1}{3}$, and according to equation (23) this can be put equal to $\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \cdot \frac{M}{d} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} N \Psi_1$; further, the molar polarisation of the solute in the vapour state is equal to $\frac{4\pi}{3} N\left(\sum \frac{\alpha_2}{3} + \frac{\mu^2}{3kT}\right)$, so that substitution in equation (25) gives

$$P_2^{\text{vap.}} = \frac{1}{f_2}\left(\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M_{1,2}}{d_{1,2}} - f_1 \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \cdot \frac{M_1}{d_1}\right) - N \Psi_1 \frac{f_1}{f_2}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right)$$
$$- \frac{\varepsilon - 1}{\varepsilon + 2} N\left(\Psi_2 + \frac{\Theta}{3kT}\right) \quad . \quad . \quad (26)$$

the first term on the right-hand side being $P_2^{\text{sol.}}$. In very dilute solutions it may be assumed that the dielectric constant and the density vary in a linear manner with the concentration, thus

$$\varepsilon = \varepsilon_1(1 + af_2) \text{ and } d_{1,2} = d_1(1 + bf_2)$$

It can then be shown [24] that in the limit as infinite dilution is approached, when the first term in equation (26) becomes ${}_\infty P_2$, the second term becomes $N \Psi_1 \frac{3a\varepsilon_1}{(\varepsilon_1 + 2)^2}$ and in the third ε becomes the value for the solvent, *i.e.*, ε_1, so that

$$P_2^{\text{vap.}} = {}_\infty P_2 - \left[N \Psi_1 \frac{3a\varepsilon_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} N \Psi_2 + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} N \frac{\Theta}{3kT}\right] . \quad (27)$$

In this equation the quantity Ψ_1 applies to the pure solvent, but Ψ_2 and Θ are those applicable to the solute molecule in a *state of infinite dilution in the solvent*, and not those for the pure homogeneous solute. Of the correction terms in the square bracket of equation (27) the first two are generally small and negative, but the third, which is the most important, can be negative or positive according as the dipole moment of the solute molecule lies along the axis of greatest polarisability or not: that is, according as the solute has a positive or negative Kerr constant, the sign of which is opposite to

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[24] **G. Hedestrand, *Z. physikal. Chem.*, 1929, *B*, 2, 428.**

that of Θ.[25] This result is, therefore, in qualitative agreement with experiment and with Higasi's treatment. By assuming the solute to be represented by an ellipsoidal cavity of the same shape as benzene, M. A. Govinda Rau [23] was able to apply equation (27) to measurements [26] on nitrobenzene in various solvents, and thereby obtained a value of P_2 in good agreement with that observed for the vapour : for dioxan as solvent, however, there was an appreciable difference. E. G. Cowley and J. R. Partington [5] have tested the equation with measurements on benzonitrile, bromobenzene, and ethyl bromide; the calculated $P_2^{\text{vap.}}$ values are of the correct order, and almost constant for data from different solvents, but they differ somewhat from the experimental vapour values. It is important to note that for carbon disulphide as solvent, the molecules of which are anisotropic, the discrepancies are considerable. The fundamental difficulty in the exact application of equation (27) lies in the evaluation of the important quantity Θ for the solute : not only is the basis of its calculation from optical and other data uncertain, but the result so obtained is for the *pure* solute, whereas, as emphasised above, it is the value at infinite dilution in the particular solvent which is required. By using experimental $P_2^{\text{vap.}}$ data Θ can be calculated, and the results so obtained are different from those evaluated for the pure solute;[27] further, the Θ values vary appreciably from one solvent to another.[28] The fundamental arguments of Raman and Krishnan, upon whose treatment Govinda Rau's equation is based, have also been subjected to criticism.[29]

(Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre,[30] following F. R. Goss,[31] have shown that the relationship

$$\frac{P_0^{\text{liq.}}}{P_0^{\text{vap.}}} = 1 + \frac{3\Theta}{4\pi\mu^2}\cdot\frac{\varepsilon - 1}{\varepsilon + 2} \quad . \quad . \quad . \quad . \quad (28)$$

may be derived from the Raman and Krishnan equation for a *pure* liquid, and there is reason to suppose that a similar equation will apply if $P_0^{\text{liq.}}$ is replaced by $P_0^{\text{sol.}}$ determined from measurements

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[25] M. A. Govinda Rau, *loc. cit.*, ref. (23), p. 505; (Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre, *J.*, 1935, 1747 (1748).

[26] M. A. Govinda Rau and B. N. Narayanaswamy, *Proc. Indian Acad. Sci.*, 1935, **1**, *A*, 489.

[27] M. A. G. Rau, *loc. cit.*, ref. (23), p. 507; F. C. Frank, *Chem. and Ind.*, 1936, **55**, 37; E. G. Cowley and J. R. Partington, *J.*, 1937, 130.

[28] R. J. W. Le Fèvre and P. Russell, *ibid.*, 1936, 491 (492); H. O. Jenkins and S. H. Bauer, *loc. cit.*, ref. (21).

[29] H. O. Jenkins and L. E. Sutton, *J.*, 1935, 609 (614); H. Müller, *Physical Rev.*, 1936, **50**, 547; H. O. Jenkins and S. H. Bauer, *loc. cit.*, ref. (21).

[30] *J.*, 1935, 1747.

[31] *J.*, 1934, 696.

in solution after extrapolation to infinite dilution. It must be pointed out, however, that the argument is not exact, since Θ, μ, and ε in equation (28) for the pure liquid refer to the same substance; when the equation is applied to a solution, however, Θ and μ refer to the solute and ε to the solvent. By making use of the equation $P_0^{\text{vap.}} = 4\pi N\mu^2/9kT$, it is seen that the relationship of Le Fèvre and Le Fèvre is identical with equation (27) with the first two terms in the square bracket omitted: it can only be regarded, therefore, as approximate. If Θ is assumed to be equal to $- 4\pi\mu^2/3$, then equation (28) becomes identical with the empirical relationship, equation (6), with K equal to unity (p. 120). By making the same assumption, M. A. Govinda Rau [32] has shown that equation (27) may be reduced to the form of equation (4) with A and B having the significance attributed to them by Sugden (see p. 119). It has been emphasised, however, by F. R. Goss [31] that it is very unlikely that Θ should be equal to $- 4\pi\mu^2/3$; this only occurs when μ is zero. Further, at the critical point Θ vanishes, whereas μ retains its normal value. Mention may be made of the fact that, even before Rau had applied the Raman–Krishnan equation to dilute solutions, F. R. Goss [33] had used it to calculate vapour dipole moments from measurements in solution: the treatment is, however, not entirely justifiable, since the same equation was assumed to apply to dilute solutions as well as to pure liquids. It should be noted that Goss, Rau, and Le Fèvre have all obtained relationships which can be written in the form of Sugden's equation (4), and by utilising the fact that μ is proportional to $\sqrt{P_0}$ they all reduce to the same type as equations (10) and (15) of Weigle and of Higasi, respectively, provided small terms are neglected: the constant factor preceding $(\varepsilon - 1)/(\varepsilon + 2)$ is in each case related to the shape of the molecule.

Apart from the modifications of the Mosotti–Clausius–Debye equation described above, attention must be called to a number of theoretical investigations; some of these have not yet reached the stage of being of practical value, but they may have an important influence on future developments. Amongst other factors, the Debye treatment neglects the force on a polar molecule due to the surrounding molecules being polarised by the molecule considered. M. Kubo,[34] E. A. Guggenheim,[35] and L. Onsager [36] have independently attempted to take into consideration what is called by Onsager the " reaction field," as distinct from the " cavity field " treated by

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[32] *Loc. cit.*, ref. (23), p. 508.

[33] *Loc. cit.*, *J.*, 1935, 502, 727; see also F. Fairbrother, *J.*, 1934, 1846.

[34] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **27**, 295.

[35] *Nature*, 1936, **137**, 459.

[36] *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

Debye, following Mosotti and Clausius. Kubo has applied his argument to gases only, and finds

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left[\alpha + \frac{\mu^2}{3kT} \left(1 + \frac{2\pi\alpha\mu^2\nu}{9kT\beta^3} \right) \right] \quad . \quad . \quad (29)$$

where ν is the number of molecules per c.c., α is the polarisability, and β is the radius of the "sphere of action" of the molecules. In a preliminary report, Guggenheim gives the result of a treatment based on the use of a model for polar solutions similar to that employed by Debye and Hückel for electrolytes: the solvent molecule is assumed to be spherical and the solvent is regarded as a continuous medium. It is deduced that

$$[(\varepsilon - \varepsilon_0)^2 - (n_0^2 - n^2)]/\varepsilon_0 = 4\pi\mu^2\nu_s/3kT \quad . \quad . \quad (30)$$

where ε and n are the dielectric constant and refractive index of the solution, and ε_0 and n_0 are the values for the solvent; ν_s is the number of solute molecules per c.c. of solution, and μ is here defined as the total electric moment between the plates of a large parallel condenser filled with the solvent containing one single molecule of solute with its polar axis normal to the plates. The values of μ obtained from equation (30) are somewhat lower than those given by the Debye formula, but the results are independent of concentration, so that the decrease of polarisation often observed with increasing concentration cannot be due to association, as has been frequently suggested (see below). According to Guggenheim, the variation of μ with solvent should be given by

$$\mu(\varepsilon_0 + \tfrac{1}{2}\varepsilon_i) = \text{constant} \quad . \quad . \quad . \quad . \quad (31)$$

where $(\varepsilon_i - 1)/4\pi$ is the polarisability per unit volume of the solute sphere. The treatment is preliminary and is only applicable to spherical molecules, for which the solvent correction should, according to the views described above, be zero. Onsager has given a somewhat fuller report of his deductions: he finds for a pure dipolar liquid

$$\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} = \frac{\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)(\varepsilon + 2)} \cdot \frac{4\pi N\mu_0^2}{3kT} \quad . \quad (32)$$

where the symbols have their usual significance, and μ_0 is the dipole moment as vapour. For a dilute solution of a polar solute in a non-polar solvent the relationship deduced is

$$\varepsilon - n^2 = \frac{4\pi\mu_0^2}{3kT} \nu_s \left[\frac{\varepsilon_1(n_2^2 + 2)}{2\varepsilon_1 + n_2^2} \right]^2 \quad . \quad . \quad . \quad (33)$$

where ε and n refer to the solution, and the subscripts 1 and 2 to the solvent and solute respectively. Further, the relationship between $\mu_{\text{sol.}}$ as measured and $\mu_{\text{vap.}}$ is given by

$$\mu_{\text{sol.}} = \frac{(2\varepsilon_1 + 1)(n_2^2 + 2)}{3(2\varepsilon_1 + n_2^2)} \mu_{\text{vap.}} \quad . \quad . \quad . \quad . \quad (34)$$

According to this equation, the solvent effect for a spherical molecule —the deductions so far only apply to such molecules—should be negative. It may be pointed out that the treatments of Guggenheim and of Onsager should lead to the same equations, and it is not yet evident why the discrepancy exists.[37] J. G. Kirkwood[38] has investigated the polarisation of a *non-polar* dielectric in a homogeneous field from the molecular point of view, and has shown that the Mosotti–Clausius equation can hold only if every molecule has the same induced moment throughout all phases of its thermal motion. Statistical calculations show that the fluctuations from the mean value of this moment lead to deviations from ideal behaviour, and it is possible to deduce the equation

$$(\varepsilon - 1)M/3d = P[1 + (1 + \gamma + \sigma)Pd/M + . \; . \; . \;] . \quad . \quad (35)$$

where P is the polarisation, γ is approximately equal to $P/4v_m$, v_m being the volume of a single molecule, and σ is a correction for anisotropy. This may be compared with the ordinary Mosotti–Clausius equation written in the form

$$(\varepsilon - 1)M/3d = P[1 + Pd/M \; . \; . \; . \;] \quad . \quad . \quad . \quad (36)$$

The treatment has not so far been extended to polar molecules.

Temperature and Concentration Effects.—Now that it is realised the polarisation of a solute frequently depends on the dielectric constant of the medium, it is possible to account for the fact that the temperature method, used for determining the dipole moment of a gas or vapour, has not been found applicable to solutions.[39] Since the dielectric constant of the solvent changes with temperature, an additional factor is introduced, and it has been found that the product P_0T, which should be constant if there were no solvent effect, often falls off steadily with increasing temperature.[40] Further, the marked decrease in polarisation sometimes observed with increasing concentration of a polar solute in a non-polar solvent, *e.g.*, nitrobenzene in benzene, and which had been attributed to association of the

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[37] Private communication from Mr. E. A. Guggenheim.

[38] *J. Chem. Physics*, 1936, **4**, 592.

[39] Cf. C. P. Smyth, *ibid.*, 1933, **1**, 247; C. P. Smyth and K. B. McAlpine, *ibid.*, 1935, **3**, 347; H. O. Jenkins, *Trans. Faraday Soc.*, 1934, **30**, 739.

[40] F. H. Müller, *Physikal. Z.*, 1934, **35**, 346; E. G. Cowley and J. R. Partington, *locc. cit.*, ref. (5).

solute,[41] is probably to be attributed almost entirely to an increase in dielectric constant. A. E. van Arkel and J. L. Snoek[42] have shown that, apart from other considerations, the Debye equation can only apply to solutions if $\nu_s\mu^2 \ll kT$, where ν_s is the number of dipole molecules per c.c.; for substances having high moments this occurs only in very dilute solution, and so it is proposed to apply an empirical correction to the Debye equation, thus

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT + c\nu_s\mu^2} \right) \quad . \quad . \quad (37)$$

where c is a constant. It can be shown[43] that this equation is virtually identical with equation (4) for the variation of polarisation with the dielectric constant of the medium. It should be noted that the remarks made above concerning association do not apply to all substances: with the alcohols, for example, it is certain that the variation of association with concentration is an important factor.[44]

Abnormal Solvent Effects.—The exceptionally high dipole moments obtained for aluminium and boron trichlorides in certain solvents[45] are undoubtedly due to the formation of compounds containing semi-polar links, and the results obtained with mixtures of halogenomethanes or -ethanes and ether, acetone, or quinoline are probably to be ascribed to some kind of association between the two constituents.[46] It is a striking fact that the dipole moment of ethylene dichloride is almost the same in a number of solvents, in spite of the possibility of free rotation, but in benzene the value is exceptionally high.[47] This may also be due to a type of attraction between solute and solvent in which other than van der Waals forces are involved. Another type of abnormality has been found in connection with the hydrogen halides;[48] the moments in solution are invariably higher

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[41] Cf. J. Rolinski, *Physikal. Z.*, 1928, **29**, 658; L. G. Davy and N. V. Sidgwick, *J.*, 1933, 281.

[42] *Trans. Faraday Soc.*, 1934, **30**, 707.

[43] J. L. Snoek, *ibid.*, p. 721.

[44] See, *e.g.*, K. L. Wolf and W. Herold, *Z. physikal. Chem.*, 1934, *B*, **27**, 58; C. Hennings, *ibid.*, 1935, *B*, **28**, 267.

[45] H. Ulich, *ibid.*, 1931, Bodenstein Festband, p. 423; H. Ulich and W. Nespital; *Z. Elektrochem.*, 1931, **37**, 559; W. Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 153.

[46] O. Hassel and A. H. Uhl, *ibid.*, 1930, *B*, **8**, 187; F. H. Müller, *loc. cit.*, ref. (2); M. Kubo, *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 1221; D. P. Earp and S. Glasstone, *loc. cit.*, ref. (12).

[47] A. E. Stearn and C. P. Smyth, *J. Amer. Chem. Soc.*, 1934, **56**, 1667; cf. also M. A. G. Rau and B. N. Narayanaswamy, *Proc. Indian Acad. Sci.*, 1934, **1**, *A*, 14; M. Kubo, *loc. cit.*, ref. (46).

[48] F. Fairbrother, *J.*, 1932, 43; 1933, 1541; *Trans. Faraday Soc.*, 1934, **30**, 862; S. Mizushima, K. Suenaga, and K. Kozima, *Bull. Chem. Soc. Japan*, 1935, **10**, 167.

than for the gas. This has been explained by postulating that the solvent brings about a change towards an ionic linkage,[49] or by assuming that there is a small displacement of the proton,[50] but F. C. Frank [51] has expressed the view that the observations are adequately accounted for by reflex induced polarisation in the hydrogen halide molecules brought about by the induced moments in the solvent. These will always act in the same direction as, and so will enhance, the primary moment. The normal solvent effect for an almost spherical molecule of hydrogen halide is in any case probably positive. The marked increase of moment of iodine chloride in solution has also been attributed to an increase in the ionic contribution to the linkage,[52] but normal solvent effects have not been entirely excluded. A number of compounds containing symmetrically situated polar groups, *e.g.*, *p*-nitrobenzene, have appreciable moments in certain solvents : this has been explained [53] by assuming that, as a result of solvent–solute forces, the moment of each group is not constant but fluctuates, independently of the other, about a most probable value. The resultant moment is then not zero, and by postulating a Gaussian distribution law [54] an expression for the effective moment of the molecule, in terms of the most probable value of the group moment, can be derived. This explanation requires the period of fluctuation to be long in comparison with the time of relaxation of the solute molecule in the electrical field, but some preliminary calculations by L. E. Sutton and F. C. Frank [55] indicate that this may not be the case. A possibility being considered by these authors is that the distribution of the solvent around the dipole is affected by the applied electrical field in such a way as to influence the measured moment.

Polar Solvents.—In the theoretical discussion of solvent effects, only non-polar solvents were considered : when the solvent is polar only a qualitative treatment is possible.[56] There are a number of results in the literature [57] which suggest that certain polar solvents may be used in the measurement of dipole moments, provided a correction is made for the dielectric constant of the medium, gener-

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[49] F. Fairbrother, *locc. cit.*

[50] J. D. Bernal, *Trans. Faraday Soc.*, 1934, **30**, 872.

[51] *Loc. cit.*, ref. (4), p. 182.

[52] F. Fairbrother, *J.*, 1936, 847.

[53] H. O. Jenkins, *ibid.*, p. 862.

[54] See S. H. Bauer, *J. Chem. Physics*, 1936, **4**, 459.

[55] Private communication from Dr. L. E. Sutton.

[56] See, *e.g.*, F. C. Frank, *loc. cit.*, ref. (2), p. 190.

[57] K. Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 57; H. O. Jenkins, *J.*, 1934, 480; 1936, 862; R. J. W. Le Fèvre *et al.*, *ibid.*, 1935, 957; 1936, 491, 496; D. P. Earp and S. Glasstone, *loc. cit.*, ref. (12), p. 1719; A. E. Stearn and C. P. Smyth, *loc. cit.*, ref. (47).

ally by an empirical procedure. It is not certain, however, that the general use of polar solvents is permissible. (Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre [58] have measured the polarisations of some non-polar compounds in polar solvents, and have obtained values of considerable magnitude, *e.g.*, a moment of 1·5 *D* is indicated for benzene in nitrobenzene solution. The observations have been interpreted in terms of induced polarisations brought about by the polar molecule of solvent, but the results must be accepted with caution until due allowance can be made in the calculations for the relatively large change in the dielectric constant of the polar solvent resulting from the addition of the non-polar solute.[59] An interesting qualitative discussion of the influence of polar solvent molecules on a polar solute is given by R. J. W. Le Fèvre: [60] if molecules may be divided approximately into two types, similar to those considered by Higasi (p. 124), according as the principal moment lies along the axis of maximum polarisability (A) or perpendicular to it (B), then it is considered that a solvent of type A will be more effective in reducing the polarisation of a solute of its own type than in increasing that of a type B molecule, and a solvent of type B will cause a smaller diminution of polarisation of an A molecule than it will increase the polarisation of one of the B type. The actual effects will depend on the polarisabilities and moments of solute and solvent, on the distance apart of the molecules in the solution, and often on internal distances between dipoles. S. G.

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[58] *J.*, 1936, 487.

[59] See D. P. Earp and S. Glasstone, *loc. cit.*, ref. (12), p. 1721.

[60] *J.*, 1935, 1747; 1936, 491.

INORGANIC CHEMISTRY.

1. ATOMIC WEIGHTS.

THE period which has elapsed since this subject was last reviewed for the Annual Reports has seen the redetermination of a number of atomic weights by chemical methods. Hönigschmid and his colleagues have published papers on radium,[1] cadmium,[2] germanium,[3] tantalum,[4] molybdenum,[5] tungsten,[6] and uranium,[7] as well as on the ratio $AgNO_3 : AgCl$,[8] and American workers have made important contributions to this subject dealing with potassium,[9] rubidium,[10] gallium,[11] carbon,[12] arsenic,[13] gadolinium,[14] and europium.[15] In addition, investigations have appeared on radiogenic lead,[16, 17] erbium,[18], terbium,[19] protoactinium,[20] chromium,[21] and neon.[22] A survey of some of this new work has appeared in the fifth [23] and the

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[1] O. Hönigschmid and R. Sachtleben, *Z. anorg. Chem.*, 1934, **221**, 65.

[2] O. Hönigschmid and R. Schlee, *ibid.*, 1936, **227**, 184.

[3] O. Hönigschmid, K. Wintersberger, and F. Wittner, *ibid.*, 1935, **225**, 81; O. Hönigschmid and K. Wintersberger, *ibid.*, 1936, **227**, 17.

[4] O. Hönigschmid and R. Schlee, *ibid.*, 1935, **225**, 64; 1934, **221**, 129.

[5] O. Hönigschmid and G. Wittmann, *ibid.*, 1936, **229**, 65.

[6] O. Hönigschmid and W. Menn, *ibid.*, p. 49.

[7] O. Hönigschmid and F. Wittner, *ibid.*, 1936, **226**, 289.

[8] O. Hönigschmid and R. Schlee, *Angew. Chem.*, 1936, **49**, 464.

[9] C. R. Johnson, *J. Physical Chem.*, 1935, **39**, 781.

[10] E. H. Archibald and J. G. Hooley, *J. Amer. Chem. Soc.*, 1936, **58**, 70, 618; E. H. Archibald, J. G. Hooley, and N. W. F. Phillips, *Trans. Roy. Soc. Canada*, 1935, [iii], **29**, III, 155.

[11] G. E. F. Lundell and J. L. Hoffmann, *J. Res. Nat. Bur. Stand.*, 1935, **15**, 409.

[12] G. P. Baxter and A. H. Hale, *J. Amer. Chem. Soc.*, 1936, **58**, 510.

[13] G. P. Baxter and L. D. Frizzell, *ibid.*, 1935, **57**, 851.

[14] C. R. Naeser and B. S. Hopkins, *ibid.*, p. 2183.

[15] E. L. Meyer and B. S. Hopkins, *ibid.*, p. 241.

[16] G. P. Baxter and C. M. Alter, *ibid.*, p. 467.

[17] F. Hecht and E. Kroupa, *Z. anorg. Chem.*, 1936, **226**, 248.

[18] O. Hönigschmid, *Naturwiss.*, 1936, **24**, 619.

[19] J. K. Marsh, *J.*, 1935, 772.

[20] A. V. Grosse, *J. Amer. Chem. Soc.*, 1934, **56**, 2501; *Proc. Roy. Soc.*, 1935, *A*, **150**, 363.

[21] F. G. Núñez, *Anal. Fis. Quim.*, 1935, **33**, 533.

[22] A. von Antropoff, *Ber.*, 1935, **68**, *B*, 2389.

[23] G. P. Baxter, O. Hönigschmid, P. Lebeau, and R. J. Meyer, *Ber.*, 1935, **68**, *A*, 73—84.

sixth [24] report of the Committee on Atomic Weights of the International Union of Chemistry, and in the forthcoming seventh report the more recent investigations will be described. In these the reader will find a complete account of the chemical methods and the data obtained in each investigation, as well as the table of approved atomic weight values for the year. It is therefore unnecessary to attempt here a complete summary, and attention will be directed only to those points which appear to be of special interest and importance.

Some of these new researches are an extension of work mentioned already [25] and lead by different ratios to the same atomic weight. For example, the ratio $TeCl_4 : 4Ag : 4AgCl$ [26] gives Te = 127·63, a result only slightly higher than that from the corresponding bromide ratios which is identical with the figure Te = 127·61 obtained from the synthesis of silver telluride.[27] Similarly, the new work on tantalum chloride [4] confirms the previous value for this element, *i.e.*, Ta = 180·88, obtained by the analysis of the bromide, which is more than 0·5 unit lower than the old value of 181·4.[28] This and similar work on niobium brings the chemical into close agreement with mass spectrograph values. The same may now be said of germanium.[3, 52] The work of Hönigschmid and Menn on tungsten and Hönigschmid and Wittmann on molybdenum presents many points of interest on account of the difficulties which had to be surmounted before anhydrous specimens of WCl_6 and $MoCl_5$ could be prepared in a highly purified state and a satisfactory procedure devised for titration with silver ion. This is the first time that a direct nephelometric comparison with silver has been used in determining the atomic weights of these two elements and the values W = 183·92 and Mo = 95·95 obtained both from chemical evidence and from the close agreement with Aston's values are probably very close to the truth.

Another interesting revision is that of the atomic weight of radium carried out by Hönigschmid and Sachtleben,[1] using as starting material 5 g. of radium bromide containing 1·17% of barium bromide lent for the purpose by the Union Minière du Haut Katanga of Brussels. The accepted value for this element was based on the ratios $RaCl_2 : 2Ag : 2AgCl$ and $RaBr_2 : 2Ag : 2AgBr$ determined by Hönigschmid in 1912 [29] with about 1 g. of the chloride supplied by the Vienna Radium Institute. The much larger amount made possible a

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[24] G. P. Baxter, O. Hönigschmid, and P. Lebeau, *J. Amer. Chem. Soc.*, 1936, **58**, 541—548.

[25] *Ann. Reports*, 1934, **31**, 95.

[26] O. Hönigschmid and H. Baudrexler, *Z. anorg. Chem.*, 1935, **223**, 91.

[27] *Ann. Reports*, 1933, **30**, 83.

[28] *Ibid.*, p. 82; 1934, **31**, 95.

[29] *Monatsh.*, 1912, **33**, 253; 1913, **34**, 283.

more elaborate purification and recrystallisation. The final material, after an extensive series of recrystallisations as chloride, was tested spectroscopically by W. Gerlach and E. Riedl [30] and found to contain a trace only of barium, estimated at 0·002—0·003%. Of this purified material 3·5 g. were obtained. Quantities varying from 2 to 3·4 g. were dried and converted into the anhydrous salt by heating in gaseous hydrogen bromide charged with bromine up to a temperature of 750°, the gas being displaced by nitrogen, and this in turn by air. After weighing, the bromide was converted into the chloride by similar treatment with hydrogen chloride and chlorine, followed by nitrogen and air—a method essentially similar to that used first by R. Whytlaw-Gray and (Sir) W. Ramsay [31] when attempting to determine the atomic weight of radium with very small amounts of material.

Difficulties were experienced in weighing the anhydrous radium salts on account of the heat evolution. The final value found for the atomic weight was 226·05, slightly higher than the older value 225·97. Success with this element has led Hönigschmid and Wittner [7] to revise earlier work carried out in Munich on the atomic weight of the parent element uranium, and in a comprehensive investigation recently published they describe the preparation of anhydrous UCl_4 and UBr_4—every precaution being taken to obtain perfectly homogeneous materials of definite stoicheiometric composition—and their subsequent analysis in terms of silver by standard methods.

The mean values for the nephelometric titrations gave U = 238·073 from the chloride and U = 238·076 from the bromide ratios.

The halides prepared from minerals from different districts and of varied geological age gave identical values for the atomic weight. Although a number of determinations were also made in which the precipitated silver halides were collected and weighed, giving values of 238·066 from the ratio $UCl_4 : 4AgCl$ and 238·088 from $UBr_4 : 4AgBr$, yet these were not considered so reliable and were rejected in calculating the final mean. Some indication was also obtained that fusion of the uranium halides before weighing led to a slight dissociation and so raised the atomic weight. All the sources of error indicated by a careful study of the data being taken into account, U = 238·07 is advanced as the most probable value, appreciably lower than the international figure 238·14.

At the end of the paper the authors discuss the bearing of their results on the uranium–radium series and the origin of actinium and are able to show that they accord satisfactorily with physical data.

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[30] *Z. anorg. Chem.*, 1934, **221**, 103.

[31] *Proc. Roy. Soc.*, 1912, *A*, **86**, 270.

Starting from uranium-lead from Morogoro, the atomic weight of which O. Hönigschmid, R. Sachtleben and H. Baudrexler found some years ago to be 206·03,[32] and which G. P. Baxter and C. M. Hilton [33] have since confirmed, they point out that this value is identical with the mass-spectrograph figure for uranium-lead [34] from the same source when the latter is corrected to the chemical standard. Aston showed that this lead contained only the isotopes ^{206}Pb(Ra-*G*) and ^{207}Pb(Ac-*D*) in the ratio of 93·1 to 6·9. The atomic weight of radium-*G* is hence 205·965, from which, by taking into account the energy changes and the α-particles lost in passing from uranium to radium and from radium to radium-*G*, they find the calculated atomic weights of uranium and radium to be 238·044 and 226·018, in satisfactory agreement with the experimentally found values of 238·07 and 226·05.

That uranium consists mainly of ^{238}U and contains no higher isotope but only something less than 1% (0·4% estimated from radioactivity measurements) of ^{235}U, the parent of protoactinium, seems certain from the work of A. J. Dempster,[35] who has recently compared in his mass spectrograph the doubly-charged ions of uranium and thorium with the two tin isotopes ^{116}Sn and ^{119}Sn.

Reducing the values to the chemical scale and taking into account the small amount of ^{235}U, he finds U = 238·028 and Th = 232·024. No indication of a higher isotope was obtained. Thus Aston's conclusion that 231 is the atomic weight of protoactinium is again confirmed. This is in accordance with a direct measurement of the atomic weight made by A. V. Grosse [36] by the conversion of K_2PaF_7 into Pa_2O_5 by evaporation with sulphuric acid, followed by precipitation with ammonia and subsequent ignition. Though the quantity of material was small (about 50 mg. of oxide), it showed no impurities when examined in an *X*-ray spectrograph, but the value 230·6 ±0·5 might well be checked later on by a standard method. Pa = 231 appears this year for the first time in the international table.

Important work on fundamental ratios has appeared during 1936 from the Munich laboratories. It has been found possible to carry out the conversion of silver nitrate into silver chloride with gaseous hydrogen chloride with the high accuracy required in this class of investigation.

It is obviously an advantage if solution, precipitation, filtration,

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[32] *Z. anorg. Chem.*, 1933, **214**, 104; see *Ann. Reports*, 1933, **30**, 34.

[33] *J. Amer. Chem. Soc.*, 1935, **57**, 469.

[34] F. W. Aston, *Proc. Roy. Soc.*, 1933, *A*, **140**, 535.

[35] *Nature*, 1936, **138**, 120, 201.

[36] *Proc. Roy. Soc.*, 1935, **150**, 363; *Ann. Reports*, 1935, **32**, 146.

transference, and the evaporation of large volumes of liquid can be avoided, and the reaction carried out in the same vessel with gaseous reagents. Dry reactions are, however, subject to errors due to a variety of effects such as adsorption and sublimation, but it is interesting to note their increasing use in modern work as exemplified by the synthesis of silver sulphide,[37] selenide,[38] and telluride,[39] the reduction of silver nitrate to silver by hydrogen,[40] the conversion of barium perchlorate into barium chloride [41] by hydrogen chloride gas, of silver iodide into silver chloride,[42] and of radium and barium bromides into the chlorides [1] in a similar way. Making use of a technique similar to that employed in the reduction of silver nitrate, O. Hönigschmid and R. Schlee [8] obtained for this ratio from eight closely concordant experiments a mean value of 1·185241 with a maximum divergence of 7 in the last decimal place. International atomic weights being used, the calculated ratio is 1·185235. Combining the new ratio with the well-established ratios $AgNO_3 : Ag = 1{\cdot}57479$ and $AgCl : Cl = 4{\cdot}042592$, the following values were obtained: $Ag = 107{\cdot}881$, $Cl = 35{\cdot}456$, $N = 14{\cdot}009$, which, taking into account the indirect method of calculation, the authors regard as a confirmation of the accepted values $Ag = 107{\cdot}880$, $Cl = 35{\cdot}457$, $N = 14{\cdot}008$, which are based on more direct ratios.

Another example of stoicheiometric work on a standard ratio is that by C. R. Johnson [9] on the atomic mass of potassium in which the experience gained in previous work on sodium [43] has now been applied to this element. The investigation on the ratios $NaCl : Ag$ and $NaCl : AgCl$ mentioned in the 1934 Report presented a number of new features, among others the checking of the equal opalescence method of nephelometric titration by potentiometric analyses. In the latest work, five samples of highly purified potassium chloride, prepared from material from American, German, and Norwegian sources, were referred to three independently purified samples of silver, and the fifteen determinations gave values for the $KCl : Ag$ ratio ranging from 0·691103 to 0·691112, giving a mean of 0·691108 ± 0·0000005, which, with international values for Ag and Cl, gave $K = 39{\cdot}100$. This lies midway between the international value

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[37] O. Hönigschmid and R. Sachtleben, *Z. anorg. Chem.*, 1931, **195**, 207.

[38] O. Hönigschmid and W. Kapfenberger, *ibid.*, 1933, **212**, 198 (see *Ann. Reports*, 1933, **30**, 82, 83).

[39] O. Hönigschmid and K. Wintersberger, *ibid.*, p. 242 (see *Ann. Reports*, *loc. cit.*).

[40] O. Hönigschmid, E. Zintl, and P. Thilo, *ibid.*, 1927, **163**, 65.

[41] O. Hönigschmid and R. Sachtleben, *ibid.*, 1929, **178**, 1.

[42] O. Hönigschmid and H. Striebel, *Z. physikal. Chem.*, Bodenstein Festband, 1936, 283.

[43] *J. Physical Chem.*, 1933, **37**, 923; *Ann. Reports*, 1934, **31**, 95.

K = 39·096, based on the work of G. P. Baxter and W. M. MacNevin[44] and of Hönigschmid and Sachtleben,[45] and the high value K = 39·104, found previously by Hönigschmid and J. Goubeau,[46] and is identical with the value for potassium appearing in the international table prior to 1934. No satisfactory reason for the cause of these small differences has so far been given, but a suggestive investigation on the ratio of the two main isotopes of this element ^{39}K and ^{41}K by A. K. Brewer[47] shows the importance of a knowledge of isotopic composition in stoicheiometric work of high accuracy. Brewer, using a mass spectrograph of considerable resolving power, has measured the $^{39}K/^{41}K$ ratio in potassium from a large number of samples of sea water and found a hardly detectable variation from the mean value 14·20; minerals exhibited a slightly greater variation ($^{39}K/^{41}K$ = 14·25), whilst in the ashes of plants a change of 15% in the ^{41}K content was found. Kelp contained the largest amount of ^{41}K. The atomic weight of potassium calculated from the sea-water ratio, probable values being assumed for the packing fraction and for the change to the chemical scale, was 39·094.

To account for a difference of 0·01 unit in the atomic weight of potassium would require the displacement of the abundance ratio of 1·1 units, which is well within the variation found in potassium of vegetable origin, but the author, after discussing the available data, rejects this explanation. Brewer's results seem well founded and are in agreement with the values for the same ratio found by A. O. Nier,[48] who finds $^{39}K/^{41}K$ = 13·96 and an atomic weight of 39·096. It may be noted that the rare isotope ^{40}K discovered recently by Nier[48a] and confirmed by Brewer[49] is probably the source of the β-radiation of potassium. The suggested degradation of ^{41}K to ^{41}Ca has been negatived by recent work of F. W. Aston,[50] who was unable to detect this isotope even in calcium separated from very old potassium minerals and which was reported to have a high atomic weight: ^{40}K is only present in small amount, and the ratio $^{39}K/^{40}K$ is estimated at about 8400/1 and would have no detectable effect on the chemical atomic weight. The atomic weight of the

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[44] *J. Amer. Chem. Soc.*, 1933, **55**, 3185.

[45] *Z. anorg. Chem.*, 1933, **213**, 365 (see *Ann. Reports*, 1933, **30**, 85).

[46] *Ibid.*, 1927, **163**, 93 (see *Ann. Reports*, *ibid.*).

[47] *J. Amer. Chem. Soc.*, 1936, **58**, 370, 365.

[48] *Physical Rev.*, 1935, **48**, 283.

[48a] *Ibid.*, 1936, **50**, 104; see also G. von Hevesy and M. Lögstrup, *Z. anorg. Chem.*, 1928, **171**, 1.

[49] *Physical Rev.*, 1935, **48**, 640; see also O. Klemperer, *Proc. Roy. Soc.*, 1935, *A*, **148**, 638; and H. J. Walke, *Nature*, 1935, **136**, 755.

[50] *Proc. Roy. Soc.*, 1935, *A*, **149**, 399; F. H. Newman and H. J. Walke, *Phil. Mag.*, 1935, **19**, 767.

closely related element rubidium has been redetermined with modern refinements by E. H. Archibald and J. G. Hooley and found to be 85·481. Nier computes the atomic weight at 85·45.

Until recently it has been assumed that the variation in isotopic composition of the elements in chemical and physical processes is, with the exception of hydrogen, too small to influence even the most accurate of atomic-weight values. Recent physical considerations, however, show that on account of isotopic exchange occurring during chemical reactions this view may require modification. H. C. Urey and L. J. Greiff [51] have calculated from spectroscopic data the equilibrium constants and enrichment factors of several exchange reactions involving isotopes of the lighter elements, and claim that in some cases the theoretical limit to precision in atomic-weight determinations has already been reached. They conclude that "the atomic weights of many common elements as determined by known chemical methods are not fundamental constants of nature to more than a limited precision." For instance, in a mixture of chlorine and hydrogen chloride, when equilibrium is established the chlorine will become richer and the hydrogen chloride poorer in the ^{37}Cl isotope to an extent which would alter the atomic weight by 0·001 unit.

So far, enrichment factors have been calculated only for a few reactions, but for some of these, experimental confirmation has been obtained, as, *e.g.*, the concentration of ^{18}O in carbon dioxide in equilibrium with water,[52] and ^{13}C from exchange between bicarbonate ion and carbon dioxide.[53]

Since oxygen is the standard of atomic weights, the question may well be asked : What isotopic composition is to be regarded as normal? Oxygen in air has been proved to be heavier than oxygen combined in water. M. Dole[54] finds a difference of 6 parts per million in the densities of the water made by combining these two oxygens with the same sample of hydrogen, whilst N. Morita and T. Titani [55] find 7 p.p.m.; that is, if water oxygen is taken as standard, air oxygen has an atomic weight of 16·00012; this difference is, however, very small, and unless chemical reactions involve a greater isotopic separation than has so far been found, it can exert no appreciable influence on atomic weights for chemical use.[56]

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[51] *J. Amer. Chem. Soc.*, 1935, **57**, 321.

[52] L. H. Webster, M. H. Wahl, and H. C. Urey, *J. Chem. Physics*, 1935, **3**, 129.

[53] H. C. Urey, A. H. W. Aten, jun., and A. S. Keston, *ibid.*, 1936, **4**, 623.

[54] *Ibid.*, pp. 268, 778.

[55] *Bull. Chem. Soc. Japan*, 1936, **11**, 414; see also C. H. Greene and R. J. Voskuyl, *J. Amer. Chem. Soc.*, 1936, **58**, 693.

[56] See also W. Bleakney and J. A. Hipple, jun., *Physical Rev.*, 1935, [ii], **47**, 800.

It does, however, seem important to have an invariable standard for chemical work, if only to be able to detect any considerable isotopic exchanges which may occur in chemical operations and also to check atomic weights from physical data. It is obviously desirable, too, that fundamental chemical ratios should be determined with material of known isotopic composition. Since the preparation and purification of chemical substances are usually carried out in aqueous solution, the isotopic ratio of oxygen in fresh water, which appears from numerous measurements from different localities to be remarkably constant, might well be taken as normal.

Turning now from chemical to physical methods, progress has been rapid in the determination of the exact masses of isotopes and the computation of atomic weights from the abundance ratios. Since the survey of the rare earths which revealed some remarkable discrepancies in the chemical values that have in some cases been explained by revision on the chemical side (terbium,[19] erbium,[18] gadolinium[14]), F. W. Aston[57] has applied his methods to titanium, zirconium, calcium, gallium, silver, nickel, iron, hafnium, indium, cadmium, carbon, thorium, and rhodium. Good agreement with chemical values was obtained for the first seven elements, the silver value agreeing within the limits of error of the instrument with the chemical. With hafnium, indium, and cadmium the agreement was not so good, and for the last element has led to a revision by chemical methods[2] which has confirmed the international value 112·41 and exceeds the physical figure by 1 part in 557. Thorium and rhodium were found to be simple elements. Recently, A. O. Nier[48a] has studied cadmium with a mass spectrograph of high resolving power, and has found somewhat different values for the proportions of the nine isotopes, leading to 112·37 for the atomic weight. Gold, one of the four elements which has withstood all Aston's attempts at analysis, has recently been resolved by A. J. Dempster.[58] He finds it to consist of only one species of atom 197, and its chemical atomic weight 197·2 is very probably too high.

One section of last year's Report[59] drew the attention of chemists to the remarkable developments in nuclear physics which enable the masses of atoms to be calculated with a surprising degree of accuracy from a knowledge of the energy changes accompanying nuclear transformations. It described how a study of the mass equivalents of the energy released when light atoms are disintegrated by proton and deuteron bombardment has brought to light an error in the mass-spectrograph value for helium which was subsequently corrected. Since then Aston,[60] using his third mass spectrograph, has obtained

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[57] *Loc. cit.*, p. 396.

[58] *Nature*, 1935, **136**, 65.

[59] *Ann. Reports*, 1935, **32**, 17, 18.

[60] *Nature*, 1936, **137**, 357, 613.

new and more accurate values for a number of isotopes, and the study of nuclear energy changes is extending with such rapidity that exact values for a large number of atomic masses will soon be available. Already a number of computations of values for the lighter atoms have been made[61-64] either from nuclear transformations alone or from a combination of the two methods. The values so obtained show a close concordance.

The great significance of the new work in the interpretation of nuclear stability and structure is dealt with in another section.

These advances promise to furnish chemistry with a table of atomic weights of an accuracy as great as, if not greater than, that attained so far in a few of the fundamental ratios. At present, however, atomic-weight values of high accuracy can be calculated only (*a*) for simple elements, (*b*) for elements whose isotopic composition has been measured with sufficient precision.[65] For example, although the atomic masses of ^{35}Cl and ^{37}Cl [66, 67] are now known with a probable error of ± 0·0008 unit, the estimated uncertainty in the latest value for the $^{35}Cl/^{37}Cl$ ratio [68] gives an error ten times as great in the atomic weight, *i.e.*, ± 0·008 unit. In addition, the change from the scale ^{16}O to that of chemical oxygen involves a slight uncertainty, for even with this element the limit of accuracy of the $^{16}O/^{18}O$ ratio is still an open question. Recent work in America [69] points to a slightly higher figure for the conversion factor (1·000275) than the usually accepted value of R. Mecke and W. H. J. Childs [70] (1·00022). The difference, however, is only about 1 part in 20,000. At the moment, on account of these uncertainties, and also because the most accurate of the chemical values are not those of the lighter elements, a comparison except in a few cases is valueless. In the appended table values for the atomic weights of helium, oxygen, deuterium, carbon, and nitrogen are given and compared with the international values. They are taken from Aston's latest measurements [60] and from H. A. Wilson's values [63] deduced from nuclear reaction energies alone without the use of mass-spectrograph results. For the mixed

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[61] M. L. Oliphant, A. E. Kempton, and (Lord) Rutherford, *Proc. Roy. Soc.*, 1935, *A*, **150**, 241.

[62] H. Bethe, *Physical Rev.*, 1935, **47**, 633.

[63] H. A. Wilson, *Proc. Roy. Soc.*, 1936, *A*, **154**, 560; see also L. Isakov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **3**, 301.

[64] T. W. Bonner and W. M. Brubaker, *Physical Rev.*, 1936, **50**, 308.

[65] O. Hahn, *Ber.*, 1936, **69**, 5.

[66] F. W. Aston, *Nature*, 1936, **138**, 1094.

[67] K. T. Bainbridge, *Physical Rev.*, 1933, **43**, 348.

[68] A. O. Nier and E. E. Hanson, *ibid.*, 1936, **50**, 722.

[69] S. H. Manian, H. C. Urey, and W. Bleakney, *J. Amer. Chem. Soc.*, 1934, **56**, 2610.

[70] *Z. Physik*, 1931, **68**, 362.

elements hydrogen, carbon, and nitrogen the isotopic ratios chosen are those which appear to be the most reliable. Mecke and Childs's conversion factor has been used.

Atomic Weights.

Element.	Mass spectrum.	Nuclear energy.	International value.
Protium, ^1H	1·00790 ± 0·00004	1·00769	—
Deuterium, D(^2H)	2·01426 ± 0·00007	2·01372	—
Hydrogen	1·00808	1·00787	1·0078
Helium	4·00303 ± 0·00016	4·00254	4·002
Carbon	12·0118	12·0118	12·00
Nitrogen	14·0080	14·0081	14·008
Fluorine	19·0003 ± 0·0006	—	19·000

H. A. Wilson's values for ^1H, D, and He appear to be on the low side. Probably the most reliable values for the atomic masses are those recently advanced by M. L. Oliphant [71] and by E. Pollard and C. J. Brasefield [72] by combining both methods. The values found by A. L. Vaughan, J. H. Williams, and J. T. Tate [73] for the isotopic ratios with a mass spectrograph were used in computing the values of nitrogen and carbon.

For the proportion of deuterium in normal hydrogen, a mean value taken from the recent researches of H. L. Johnston,[74] of N. F. Hall and T. O. Jones,[75] and of N. Morita and T. Titani [76] was used, which gave H/D = 5550/1. The higher value for ^1H explains to a great extent the discrepancy between the chemical and the mass-spectrograph atomic weights mentioned in the 1934 Report.[77] The international value is based on results obtained with electrolytic hydrogen, and hence of low deuterium content—probably about 1 part in 25,000.[78, 56]

It has been recognised for some years that the chemical value for carbon approximates to 12·01. The new physical values confirm this, and are in close agreement with W. Cawood and H. S. Patterson's determinations of the limiting density of ethylene and of carbon dioxide, which lead to 12·0108. A full account of this work, which gives as well as carbon, nitrogen = 14·007 and fluorine = 18·996, has now appeared.[79] It may be noted that the value for carbon

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[71] *Nature*, 1936, **137**, 396.

[72] *Ibid.*, p. 943.

[73] *Physical Rev.*, 1934, [ii], **46**, 327.

[74] *J. Amer. Chem. Soc.*, 1935, **57**, 484.

[75] *Ibid.*, 1936, **58**, 1915.

[76] *Bull. Chem. Soc. Japan*, 1936, **11**, 404.

[77] *Ann. Reports*, 1934, **31**, 98.

[78] W. Bleakney and A. J. Gould, *Physical Rev.*, 1933, **44**, 265; see also E. Moles, *Anal. Fis. Quim.*, 1935, **33**, 721.

[79] *Phil. Trans.*, 1936, *A*, **236**, 77.

becomes 12·008 if Aston's value of 140/1 is taken for the $^{12}C/^{13}C$ ratio instead of the value 91·6/1 of Vaughan, Williams, and Tate.

E. Moles [80] and his collaborators contend that C = 12·009 is a closer approximation, and some very interesting though preliminary work by G. P. Baxter and A. H. Hale [12] on combustions in oxygen of the aromatic hydrocarbons chrysene, pyrene, triphenylbenzene, and anthracene supports this figure.

R. W.-G.

2. Fluorine and its Compounds.

When Moissan isolated fluorine in 1896 he opened a new chapter in inorganic chemistry, for the new element had many curious properties and above all, an amazing reactivity unique amongst the chemical elements. Moreover, it was soon realised that this new substance could produce compounds of the highest theoretical value. For forty years this element has continued to excite the liveliest interest, and quite recently A. Damiens [1] and O. Ruff,[2] distinguished workers in the field of fluorine chemistry, have each told the fascinating story of fluorine and its compounds as it stands to-day. Although in previous Reports references have been made to isolated discoveries as they have arisen, the Reporters consider that no apology is needed for bringing together now, as a connected account, some of the important facts about fluorine and its derivatives.

The demand for the element itself has led to the elaboration of new methods of preparation, with the result that the original method of Moissan is now very little used. Nevertheless, in surveying these new methods it will be noticed that they are all based on Moissan's fundamental idea of making hydrogen fluoride electrolytically conducting by the addition of an appropriate metallic fluoride, and differ from it only in the proportions and nature of the fluoride added. It will be recalled that Moissan's process required a platinum or copper vessel with platinum electrodes and a solution containing 1 g.-mol. of potassium fluoride to 12 or more g.-mols. of hydrogen fluoride cooled to — 30°. Nowadays two main processes are in use. The first employs the molten acid fluoride, KHF_2 (m.p. 227°), in an apparatus of copper,[3] graphite,[4] silver,[5] magnesium,[6] or Monel

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[80] *Monatsh.*, 1936, **69**, 342.

[1] *Bull. Soc. chim.*, 1936, [v], **3**, 1.

[2] *Ber.*, 1936, **69**, [*A*], 181.

[3] W. L. Argo, F. C. Mathers, B. Humiston, and C. O. Anderson, *J. Physical Chem.*, 1919, **23**, 348; K. C. Denbigh and R. Whytlaw-Gray, *J. Soc. Chem. Ind.*, 1934, **53**, 139.

[4] F. Meyer and W. Sandow, *Ber.*, 1921, **54**, 759; F. Fichter and K. Humpert, *Helv. Chim. Acta*, 1926, **9**, 467.

[5] K. Fredenhagen, D.R.-P., 1928, 493,873.

[6] N. C. Jones, *J. Physical Chem.*, 1929, **33**, 801.

metal,[7] using a graphite anode, as first proposed by Mathers and his collaborators in America.[3] The second process, due to P. Lebeau and A. Damiens,[8] uses the salt KF,3HF (m.p. 65°) as electrolyte in a copper apparatus with an anode of iron or preferably nickel. K. Fredenhagen [9] advocates the use of an electrolyte containing 1 g.-mol. of potassium fluoride to about 1·8 g.-mols. of hydrogen fluoride, whilst F. C. Mathers and P. T. Stroup [10] have found a system approximating to CsF,2HF (m.p. 19°) as a satisfactory electrolyte in a magnesium cell. There is a marked difference between the type of cell employed by some workers and that used by Moissan. For example, Moissan's U-shaped copper or platinum vessel is replaced in Lebeau's [8] process by a cylindrical vessel of copper, magnesium or Monel metal with a copper or magnesium diaphragm. Mathers's process,[3] likewise, uses a cylindrical vessel of graphite, copper or magnesium with a diaphragm. In the electrolysis the fluorine never separates from the anode without some alteration of the anode surface. When platinum was employed as anode in Moissan's apparatus, a layer of platinous fluoride was formed, and over it the platinic salt. The latter dissolved in the fluoride bath, with formation of the difficultly soluble K_2PtF_6, so that appreciable quantities of platinum were lost in this way (about 5—6 g. of platinum for 1 g. of fluorine produced [2]). In Lebeau's apparatus a layer of nickel fluoride forms on the nickel anode, but this is so thin that a *P.D.* of 6 volts may be employed. Here again, in fluorine liberation an intermediate formation of a higher fluoride, possibly NiF_3, may take part. When graphite is employed as an anode, fluorine is absorbed on the surface and causes an expansion of the crystal lattice of the graphite.[11] As a result, the *P.D.* in special circumstances may increase from 8 to 110 volts. Thereby the anode temperature rises until finally an almost explosive decomposition of the surface layers again frees the surface. W. T. Miller and L. A. Bigelow,[12] using a heavy nickel U-tube and graphite electrodes, with potassium bifluoride as electrolyte, have recently shown that fluorine of 94—99% purity can be obtained.

Amongst the remarkable compounds which fluorine forms with other elements those with the halogens are of considerable interest. N. V. Sidgwick has discussed these interhalogen compounds in a previous Report,[13] and it will be found that if the halogen combining

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[7] W. C. Schumb and E. L. Gamble, *J. Amer. Chem. Soc.*, 1930, **52**, 4302.

[8] *Compt. rend.*, 1925, **181**, 917.

[9] K. Fredenhagen and O. T. Krefft, *Z. Elektrochem.*, 1929, **35**, 670.

[10] *Trans. Electrochem. Soc.*, 1934, **66**, 113.

[11] See ref. 30.

[12] *J. Amer. Chem. Soc.*, 1936, **58**, 1585.

[13] *Ann. Reports*, 1933, **30**, 128.

with fluorine is its neighbour, then this halogen has covalencies of one and three (ClF, ClF_3). If, however, one member of the series separates the combining halogens, covalencies of 1, 3 and 5 are shown (BrF, BrF_3, BrF_5), and finally when two members intervene a covalency of seven is attained (IF_7). Much of the data relating to these substances is based on the masterly researches of O. Ruff and his collaborators.

In recent years three oxygen fluorides OF_2,[14] O_2F_2,[15] and OF[15] have been prepared and their properties described, but the question whether oxy-acids of fluorine exist or not is still under discussion. It is noteworthy that although OF_2 is very slightly soluble in water, yet it fails to produce hypofluorous acid. It must not be inferred from this, however, that the acid cannot exist. It should be remembered that hyponitrous acid ($H_2N_2O_2$) is well known, yet it cannot be synthesised from water and nitrous oxide. The reaction of OF with water has not been fully investigated, and as O_2F_2 is only stable below — 64°, a consideration of its action with water does not arise. L. M. Dennis and E. G. Rochow[16] have examined the action of fluorine on a concentrated solution of sodium hydroxide at — 20° and obtained a solution which is relatively stable, liberates iodine from potassium iodide, and has a high oxidising power which is not due to potassium ozonate, ozone, hydrogen peroxide, or the oxygen fluoride OF_2. They express the opinion that it contains either hypofluorous acid or more probably fluoric acid. Moreover, these workers state that by the electrolysis of a molten mixture of potassium hydroxide and fluoride in a silver crucible with a carbon anode, they have isolated a silver salt which has the formula $AgFO_3$. However, G. H. Cady[17] does not accept the interpretation which Dennis and Rochow place upon their experiments, and suggests an alternative explanation which does not involve the existence of any oxy-acids of fluorine. Ruff[2] considers that the silver salt may be the complex compound $AgOF_3$.

The literature contains references to a number of sulphur fluorides: SF_6, SF_4, SF_2, S_2F_2, S_2F_{10}. That SF_6 exists is incontestable, for it has been prepared and its properties examined by a number of investigators since H. Moissan and P. Lebeau[18] obtained it from the reaction between sulphur and fluorine. Moreover, there is no doubt that S_2F_{10} is another product of this reaction.[19] This is proved by its molecular weight of 256. In the case of the other fluorides, how-

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[14] P. Lebeau and A. Damiens, *Compt. rend.*, 1927, **185**, 652.

[15] O. Ruff and W. Menzel, *Z. anorg. Chem.*, 1933, **211**, 204.

[16] *J. Amer. Chem. Soc.*, 1933, **55**, 2431.

[17] *Ibid.*, 1934, **56**, 1647.

[18] *Compt. rend.*, 1900, **130**, 865.

[19] K. G. Denbigh and R. Whytlaw-Gray, *J.*, 1934, 1347.

ever, the published data are very confusing. Ruff [2] and his collaborators in 1905 attempted to prepare lower fluorides of sulphur by the reaction between sulphur nitride, N_4S_4, and hydrogen fluoride, but without success, and they were also unsuccessful when they tried to decompose sulphur chlorides with certain fluorides. Twenty years later, however, O. Ruff and E. Ascher [2] observed the formation of a gas from cobaltic fluoride and sulphur, and a detailed investigation led J. Fischer and W. Jaenckner [20] to the conclusion that the liberated gas was SF_4. Their analysis gave $S : F = 1 : 3{\cdot}8$ or $3{\cdot}9$, and a molecular weight 107 (SF_4 requires 108). Unfortunately, this result was not reproducible, but a very recent re-examination of the reaction by W. Luchsinger [21] has clarified the matter. He has shown that pure SF_4 is not liberated, and that in all reactions of metallic fluorides and sulphur, the fluorides SF_6, SF_4, S_2F_2, and often also SF_2 result in varying proportions according to the kind and amount of the metallic fluoride and the velocity of the reaction. The lower fluorides S_2F_2 and SF_2 can be removed from the reaction products by shaking with mercury, the SF_6 can then be fractionated out, and the gas which remains is practically pure SF_4. This constitutes the evidence for SF_4. What data are available for the lower fluorides ? In 1923 M. Centnerszwer and C. Strenk [22] obtained a colourless gas from the reaction between silver fluoride and sulphur. It had a varying molecular weight (93—98) depending on the temperature of the reaction, and it contained S, 64; F, 35 (S_2F_2 requires S, 62·8; F, 37·2%). Although, as the authors say, " the agreement is not ideal," yet they conclude that their substance is disulphur difluoride. Recently, M. Trautz and K. Ehrmann [23] have repeated this work and isolated a gas with a molecular weight of 98·8 and containing S, 60·98; F, 39·54%. They consider that their product is a mixture of two fluorides : S_2F_2, 90%, and SF_2, 10%. Up to the present, therefore, the experimental evidence shows that no one has handled either pure S_2F_2 or pure SF_2. Ruff [2] states that he and his collaborators have obtained a gas containing 90—95% of S_2F_2, but it is decomposed by light with the separation of sulphur and the formation of SF_2. Moreover, the exceptional reactivity of both these fluorides, even with the quartz of the walls of the containing vessels, rendered isolation of the pure gases impossible. Ruff [2] is of opinion that pure S_2F_2 and pure SF_2 will be obtained if the experimental work is conducted exclusively in platinum vessels.

[20] *Z. angew. Chem.*, 1929, **42**, 810.
[21] Diss., Breslau, 1936.
[22] *Ber.*, 1923, **56**, 2249; 1925, **58**, 914.
[23] *J. pr. Chem.*, 1935, [ii], **142**, 79.

Many attempts have been made to bring about direct combination of fluorine and nitrogen, but so far without success. Nevertheless, in 1928 O. Ruff, J. Fischer, and F. Luft[24] succeeded in isolating NF_3 as a colourless gas (b.p. — 120°) by the indirect method of electrolysing NH_4HF_2. The yield of NF_3 was small and it was accompanied by small quantities of NH_2F, some NHF_2, and possibly a second nitrogen fluoride NF_2. These compounds, when associated with NF_3, apparently bestow on the trifluoride explosive properties, for if the crude gas is led over manganese dioxide the explosive compounds are destroyed and the NF_3 is quite stable. In this respect NF_3 offers a marked contrast to the highly explosive NCl_3. Whenever NF_2 or NHF_2 was present under a pressure higher than *ca.* 350 mm. it exploded, and Ruff[2] emphasises that these substances have not yet been obtained pure in spite of prolonged research. He also states that the claims of O. T. Krefft[25] to have prepared pure NH_2F cannot be admitted. Nitrogen trifluoride is very reactive and when sparked with hydrogen a shattering explosion takes place,

$$2NF_3 + 3H_2 = N_2 + 6HF + 336K,$$

and with water vapour a flame travels through the reaction vessel, filling it with deep brown fumes,

$$2NF_3 + 3H_2O = 6HF + N_2O_3.$$

In 1890 Moissan described several fluorides of carbon, obtained by the direct union of the elements, but it is only in the last decade that pure compounds have been isolated.[26, 27] On passing fluorine over carbon, spontaneous combination takes place with considerable development of heat. The gaseous products of the reaction are cooled in liquid air and subsequently fractionated, whereby the following have been obtained: CF_4, C_2F_6, C_3F_8, and other homologues up to C_6F_{14}. These carbon fluorides are extremely stable to heat and most chemical reagents. Even moderately heated sodium does not decompose them. An ethylene analogue, C_2F_4, has also been identified[28] in the reaction products; and this is also formed when carbon tetrafluoride is repeatedly subjected to an electric arc discharge between carbon electrodes. It forms $C_2F_4Br_2$ with bromine-water; but, apart from such reactions, which depend upon its unsaturated character, it is very indifferent to most reagents. A solid compound, carbon monofluoride,[29] CF, is also formed during

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[24] *Z. anorg. Chem.*, 1928, **172**, 417.

[25] D.R.P., 1932, 448,929.

[26] P. Lebeau and A. Damiens, *Compt. rend.*, 1926, **182**, 1340.

[27] O. Ruff and R. Keim, *Z. anorg. Chem.*, 1930, **192**, 249.

[28] O. Ruff and O. Bretschneider, *ibid.*, 1933, **210**, 173.

[29] F. Ebert, see *idem, ibid.*, 1934, **217**, 1.

the interaction of fluorine and carbon, particularly at low pressures and high temperatures, *e.g.*, carbon in the form of norit at 420° and 25 mm. or of graphite at 420° and 760 mm. The maximum yield in relation to the other fluorides is about 3% of the carbon converted. Carbon monofluoride is a grey solid, insoluble in ordinary solvents and indifferent to most reagents. It can, however, be reduced by zinc dust and acetic acid, yielding the original form of carbon from which it was derived.

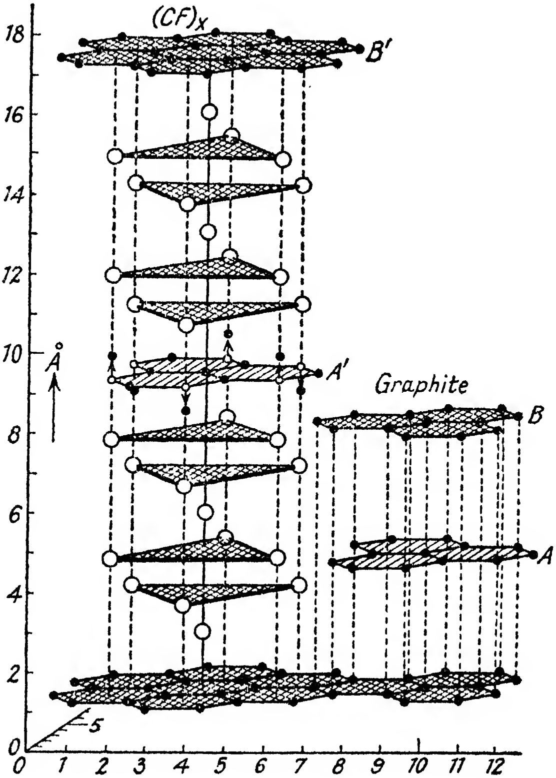

FIG. 1.

The *X*-ray analysis [29] (Fig. 1) shows that the introduction of the fluorine atoms takes place without any appreciable alteration in the distance of the carbon atoms in the basic planes of the graphite lattice. The insertion of the fluorine atoms, however, occurs between the basic planes and expands the carbon lattice in a perpendicular direction from 3·40 A. to 8·17 A. On regeneration, it shrinks to its original size. This enormous distortion of the lattice is sometimes the cause of an explosion in the formation of CF, and the authors [29] have investigated the conditions for its avoidance. It is not surprising, therefore, that carbon monofluoride is formed when carbon electrodes are used as anodes in the electrolysis of fluorides, and considerable expansion is usually observed.[30] The specific electrical resistance of CF is over 3000 ohms as compared with 0·03 ohm for graphite, and considerable passivity effects are thereby set up. O. Ruff [31] considers that the structure of carbon monofluoride closely resembles that of graphite oxide, described by U. Hofmann,[32] in which oxygen atoms are inserted between the carbon basic planes of graphite.

Amongst interesting new metallic fluorides the isolation of ReF_6 has already been mentioned in an earlier Report,[33] but attention should be directed to an investigation undertaken with the object of isolating a higher fluoride of copper and silver.[34] No fluoride of copper higher than CuF_2 could be prepared, but the existence of AgF_2 is now well established.[35] This compound has been prepared by the action of fluorine at 150—200° on a silver halide, or molecular silver prepared by reducing silver oxide with formaldehyde, or on fine silver gauze. It is a dark brown powder which with water gives oxygen containing ozone. The fluorine is relatively firmly bound, for only at 440° does the dissociation pressure of argentic fluoride reach 1 atmosphere. This fluoride is strongly paramagnetic, as is to be expected from its electronic structure. It is an excellent fluorinating agent and in many cases can act as a substitute for fluorine.

Some extraordinary mistakes by earlier observers are disclosed in recent publications on the acid fluorides of the metals. In 1905, E. Böhm [36] recorded the preparation of acid fluorides of cobalt, nickel, and copper of the general formula $MF_2,5HF,5$ or $6H_2O$. Sixteen years later, F. H. Edminster and H. C. Cooper [37] published their conclusions from a reinvestigation of these substances. They stated that the correct formula was $MF_2,5HF,6H_2O$, where M could be Co, Ni, Cu, or Mn, but added that "It was a surprise to obtain the acid fluoride by recrystallisation from water." However, a

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[30] See ref. 11.

[31] *Angew. Chem.*, 1933, **47**, 739.

[32] *Ber.*, 1932, **65**, 1821; U. Hofmann, A. Frenzel, and E. Csalán, *Annalen*, 1934, **570**, 1.

[33] *Ann. Reports*, 1933, **30**, 91.

[34] O. Ruff and M. Giese, *Z. anorg. Chem.*, 1934, **219**, 143.

[35] *Idem, ibid.*; M. S. Ebert, E. L. Rodowskas, and J. C. W. Frazer, *J. Amer. Chem. Soc.*, 1933, **55**, 3056; *Naturwiss.*, 1934, **22**, 561.

[36] *Z. anorg. Chem.*, 1905, **43**, 326.

[37] *J. Amer. Chem. Soc.*, 1920, **42**, 2419.

recent investigation by A. Kurtenacker, W. Finger, and F. Hey[38] leads to a very different conclusion. They find that the so-called acid fluorides of the type $MF_2,5HF,xH_2O$ do not exist, but that they are really fluosilicates and must be eliminated from the literature. The story, however, does not end here. According to an early investigator, I. E. Willm,[39] an acid fluoride $HTlF_2$ exists, but in 1920 J. Barlot[40] re-examined the compound and concluded that it was H_2TlF_3. O. Hassel and H. Kringstad[41] then took up the matter in 1932 and proved that the formula was really $H_2TlF_3,0{\cdot}5H_2O$, and that the substance was isomorphous with a compound $H_2(NH_4)F_3,0{\cdot}5H_2O$ which they prepared. This year C. Finbak and O. Hassel[42] published an account of a reinvestigation of a number of so-called acid fluorides. They agree with Kurtenacker and his collaborators that the recorded acid fluorides of nickel, cobalt, manganese, and copper are really fluosilicates and, what is particularly interesting, find that the acid fluorides of thallium also do not exist but are actually fluosilicates. Moreover, a mercurous compound $Hg_2F_2,4HF,4H_2O$, described by E. Böhm[36] in 1905, is found to be $Hg_2SiF_6,2H_2O$. It is obvious that the greatest care is necessary in investigations where hydrofluoric acid is employed.

It is noteworthy that quite recently J. Meyer and W. Taube[43] state that they have prepared $RbHF_2$ and RbH_2F_3, but that these substances are commonly contaminated with fluosilicates.

Attention should be directed to an ingenious method for determining critical temperatures which has been applied with success to anhydrous hydrogen fluoride by P. A. Bond and D. A. Williams.[44] A tube of Monel metal is charged with the pure hydrogen fluoride and heated in an air-bath above its critical temperature. This tube, in an inclined position, is mounted on knife edges and connected at one end by a fine platinum wire to the beam of a balance. The system is then cooled slowly and the critical temperature is clearly indicated by a sudden change in the balance-beam when the continuous phase passes to a system of vapour and liquid, with consequent displacement of the centre of gravity. The critical temperature thus determined is 230·2°.

S. R. C.
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[38] *Z. anorg. Chem.*, 1933, **211**, 83.
[39] *Ann. Chim. Phys.*, 1865, [iv], **5**, 5.
[40] *Compt. rend.*, 1920, **171**, 1143.
[41] *Z. anorg. Chem.*, 1932, **208**, 382.
[42] *Ibid.*, 1936, **226**, 175.
[43] *Ibid.*, 1936, **227**, 337.
[44] *J. Amer. Chem. Soc.*, 1932, **54**, 129.

3. Metallic Carbides.

Results of great value have been obtained during recent years by the application of *X*-ray methods to the structure of the carbides. These substances have long presented a problem in molecular structure of the very highest interest, for the attention of chemists has always been arrested by the extraordinary differences in behaviour exhibited by the metallic carbides in their reactions both with water and with acids. In certain cases the reaction products are of unexpected complexity, and many explanations have been advanced to account for these results.

There is evidently some connection between the behaviour of a carbide and its position in the periodic table. Those of the first and second groups, with the exception of beryllium carbide, give with water, acetylene only. Beryllium carbide, Be_2C, and aluminium carbide, Al_4C_3, yield pure methane, but manganese carbide, Mn_3C, gives a mixture of methane and hydrogen in equal volumes. Carbides of yttrium, lanthanum, cerium, and the other rare earths, also those of uranium and thorium, are attacked by water and yield a complex mixture of gaseous, liquid, and sometimes solid hydrocarbons.

In seeking an explanation of these results some early workers on the carbides did not hesitate to represent them by graphic formulæ, but others, more cautious, endeavoured to reconcile the formulæ of the carbides with the valency of the constituent elements. During recent years, as a result of the work of M. von Stackelberg and his collaborators, the constitution of a number of metal carbides has been disclosed by the use of *X*-ray methods, and the relationship between chemical reaction and structure made clear for the first time.

The well-known reaction of calcium carbide with bromine, and further, its decomposition with water, have convinced chemists that in this carbide the two atoms of carbon must be joined :

$$CaC_2 + 4Br_2 = CaBr_2 + CBr_3{\cdot}CBr_3$$

In 1930 von Stackelberg [1] studied the acetylides of the alkali metals, and the carbides of the alkaline-earth metals and the rare-earth metals. The structure which he finally assigned to CaC_2, UC_2, LaC_2, PrC_2, and NdC_2 is most conveniently described as a face-centred cubic lattice or sodium chloride lattice made up of metal atoms and C_2 groups.

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[1] *Z. physikal. Chem.*, 1930, *B*, **9**, 437.

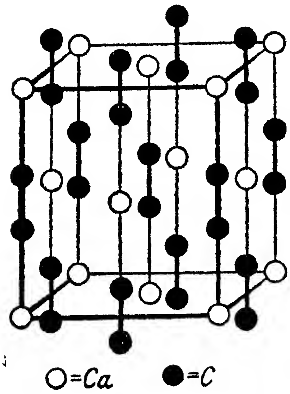

Fig. 2.

As Fig. 2 shows, the C_2 groups are all arranged parallel to one edge of the cube, which is thereby extended in this direction. The distortion may be expressed by an axial ratio c/a of 1·15—1·20. It is not surprising, therefore, that acetylene is liberated as a primary product from the decomposition with water, for already in the crystal lattice a C·C bond is present. From the fact that acetylene is the sole gaseous product in the case of calcium carbide, it must be concluded that the energy conditions are favourable for the evolution of this gas. With the carbides of uranium and of the rare earths, acetylene is evolved but it is accompanied by saturated and unsaturated hydrocarbons of great complexity. The composition (%) of the gases evolved from some of these carbides is given by H. Moissan [2] as follows :

	La.	Ce.	Pr.	Nd.	Sm.	Y.	Th.
C_2H_2	71	75·5	67·9	66·3	70·6	71·7	47·7
C_2H_4	1·5	4·2	3·0	6·3	7·9	4·6	5·8
CH_4	27·9	20·3	29·1	27·6	21·5	18·9	29·4
H_2	—	—	—	—	—	4·7	17·1

Later investigations,[3] whilst not confirming these analytical results in detail, have only served to emphasise the complexity of the gaseous mixtures. In a recent communication N. G. Schmahl [4] has put forward a theory of carbide hydrolysis based on these results of Moissan. Schmahl considers that the following reaction occurs in the decomposition of the rare-earth metal carbides by water :

$$4XC_2 + 6H_2O = 2X_2O_3 \text{ (hydrated)} + 3C_2H_2 + CH_4 + CH_2$$

According to Schmahl this CH_2 radical is changed into ethylene and propylene or to methane and ethane, depending on the heat of the reaction. J. Schmidt [5] has examined this suggestion, and pointed out that Schmahl's theory demands the formation of acetylene and methane in a ratio 3 : 1, which would be lowered in those cases where the CH_2 radical is reduced to methane. Actually, if the figures

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[2] *Ann. Chim. Phys.*, 1896, [vii], **9**, 302.

[3] A. Damiens, *Compt. rend.*, 1913, **157**, 214; P. Lebeau and A. Damiens, *ibid.*, **156**, 1987.

[4] *Z. Elektrochem.*, 1934, **40**, 68.

[5] *Ibid.*, p. 170.

given by Moissan are examined, it will be seen that the ratio $C_2H_2 : CH_4$ is sometimes greater than 3 and sometimes less. Above all, however, Schmahl's theory fails to recognise that in the crystal lattice a C–C bond is already present. In Schmidt's view the suggestion of Schmahl is untenable, and there appear sound grounds for this conclusion. Instead, Schmidt considers that the difference in the reaction products from calcium carbide and the rare-earth metal carbides is due to the different valencies of the metal atoms. If the metal atom, M, is bivalent, as in calcium carbide, then the carbon is bound as acetylene and the metal as the hydroxide $M(OH)_2$. If, however, the metal is in the tervalent state, hydrogen is liberated, and it is the further reactions between the acetylene and this hydrogen which produce the complicated mixture of hydrocarbons. Schmidt is of opinion that methane itself is a side product of such reactions. He considers that his views are supported by the carbides of the tervalent elements aluminium and cerium. Carbides of these elements can be prepared of the general formula $X_2(C \equiv C)_3$ in which the metal atom has a valency of three.[6] On hydrolysis, acetylene alone is liberated, because the metal atoms concerned do not undergo a valency change but are stable as $Al(OH)_3$ and $Ce(OH)_3$. Reference to the preceding table will show that the composition of the gaseous products from the hydrolysis of thorium carbide, ThC_2, offers a striking contrast to that from the other carbides included. It might be anticipated, therefore, that this difference in chemical behaviour would be reflected in the structures of these carbides, and it is interesting to find that this is so. The structure of ThC_2 (Fig. 3), although similar to that of the

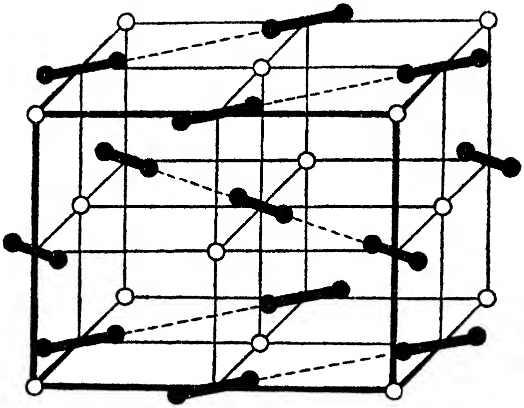

FIG. 3.

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[6] J. F. Durand, *Bull. Soc. chim.*, 1924, **35**, 1141; L. Damiens, *ibid.*, 1914, **15**, 370.

CaC_2 type, has the C_2 groups all parallel to a cube face but with their axes in two mutually perpendicular directions. The distortion produced gives rise to a tetragonal lattice with an axial ratio $c : a = 0{\cdot}903$.

Particularly interesting are the detailed structures which have been evolved for the carbides of aluminium and beryllium, Al_4C_3 and Be_2C, for they explain in a most convincing way why methane is the sole hydrocarbon produced by hydrolysis. Beryllium carbide, Be_2C,[7] has been shown to have an antifluorite structure, in which each beryllium atom is surrounded by four carbon atoms and each carbon atom has eight beryllium atoms as neighbours. The C–C distance is 3·06 A., and Be–C is 1·9 A. This separation of the carbon atoms in the crystal lattice, combined with the bivalency of the beryllium atoms, explains most effectively why methane results from the hydrolysis. The detailed structure of aluminium carbide [8] is complicated, and is best understood by reference to the diagrams in the original publication. However, it can be described as a layer lattice in which three layers of carbon atoms are interleaved with four layers of aluminium atoms so that each unit has the composition $(Al_4C_3)_\infty$ and is, in itself, saturated with regard to valency. Each aluminium atom is surrounded by four carbon atoms at a distance of 1·9—2·0 A., while the carbon atoms have either 5 or 6 aluminium atoms as neighbours. With such a structure the formation of methane, by hydrolysis of the carbide, would be expected. It is well established that hydrogen and a number of hydrocarbons are produced when either Ni_3C or Fe_3C is treated with hydrochloric acid. To explain this result, J. Schmidt [5] assumes that the CH_2 group is formed initially, and it then undergoes hydrogenation to methane or polymerisation to ethylene. This ethylene can then be further changed by hydrogenation or renewed polymerisation or reaction with a new CH_2 group. In the decomposition of Fe_3C, polymerisation must occur to a marked degree, for in addition to gaseous hydrocarbons, liquid and solid hydrocarbons may be formed.[9] H. A. Bahr and T. Bahr [10] state that they observed the formation of liquid hydrocarbons in the decomposition of Ni_3C with hydrochloric acid, but J. Schmidt could not confirm this. Incidentally, the decomposition of Fe_3C is complicated by the separation of elementary carbon, which is accelerated by ferrous ions.[11] A carbon separation can also take place when Ni_3C is decomposed, but it has

[7] M. von Stackelberg and F. Quatram, *Z. physikal. Chem.*, 1934, *B*, **27**, 50.

[8] M. von Stackelberg and E. Schnorrenberg, *ibid.*, p. 37.

[9] E. D. Campbell, *Amer. Chem. J.*, 1896, **18**, 836.

[10] *Ber.*, 1928, **61**, 2177.

[11] R. Schenck and R. Stenkhoff, *Z. anorg. Chem.*, 1927, **161**, 287.

not yet been demonstrated that it can be influenced by concentration of nickel ions.[5]

An *X*-ray investigation of these carbides does appear to throw some light on their behaviour with acids, for it indicates that the individual carbon atoms in the lattice of Fe_3C and Ni_3C [12] are separated from one another, and this implies the possibility of the formation of a primary CH_2 group. This is especially so in Fe_3C, for its method of preparation and its existence in equilibrium with iron (ferrite) indicate that the metal in the carbide is in the lower state of oxidation, *i.e.*, bivalent. By analogy one might assume a similar method of decomposition for Mn_3C but, as is well known, methane and hydrogen are the only products. The crystal structure of Mn_3C is not known accurately, but evidently it must be fundamentally different from that of Fe_3C. F. Fischer and F. Bangert [13] have prepared a manganese carbide of a different type by the reaction of manganese oxide and methane. When it was decomposed with water, the evolved gas contained 2·5% of unsaturated hydrocarbons, 45% of saturated hydrocarbons, and 52·5% of hydrogen. The unsaturated hydrocarbons contained on an average at least four carbon atoms. This carbide agrees with the formula $(Mn_5C_2)_6$. A. Westgren [14] has recently examined the crystal structure of a manganese carbide to which he assigns the composition Mn_7C_3. A magnesium carbide, Mg_2C_3, is known to give pure allylene $CH_3 - C \equiv CH$ on hydrolysis but its crystal structure is unknown.[15] The fact that only one hydrocarbon is formed suggests, by analogy with the carbides of the CaC_2 type, that the C–C–C bond is already present in the crystal lattice.

S. R. C.
W. W.

4. CO-ORDINATION COMPOUNDS.

The old idea that the term co-ordination compound is restricted to the well-known cobalt, chromium, and platinum ammines is undoubtedly disappearing, and it is being realised that these complex salts represent only a special section of an exceedingly wide and diverse class of substances. In an introduction to the symposium on complex inorganic compounds arranged by the American Chemical Society, L. F. Audrieth [1] pointed out how recent develop-

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[12] B. Jacobsen and A. Westgren, *Z. physikal. Chem.*, 1933, *B*, **20**, 361; J. Schmidt, *Z. anorg. Chem.*, 1933, **216**, 85.

[13] *Brennstoff-Chem.*, 1929, **10**, 261.

[14] *Jernk. Ann.*, 1935, **118**, 231.

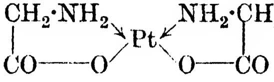
[15] See N. G. Schmahl, ref. (4).

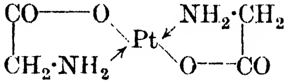
[1] *Chem. Reviews*, 1936, **19**, 55.

ments in theoretical chemistry and in research technique had given new prominence to this field of investigation. The Brönsted concept of acid–base equilibria has directed attention to complex ions in the development of acidic and basic properties in solution, whilst the ever-changing theories of atomic structure have demanded investigation of the physical and chemical properties of compounds characterised by the covalent link. Interest in the modern theories of optical activity has stimulated investigations of the optical properties of complex inorganic compounds, whilst improved apparatus and the development of new research technique, such as are available in *X*-ray and electron-diffraction methods and in measurements of dipole moments, have thrown a flood of light on the detailed structure of co-ordination compounds.

A few years ago it was quite true to say that the available evidence indicated that the arrangement of the valencies of 4-covalent atoms was almost always tetrahedral. This was the general conclusion arrived at by the classical methods of stereochemistry and it was supported by a substantial mass of physical data. In the discussion on modern stereochemistry, held by the Chemical Society, S. Sugden[2] reviewed recent work on 4-covalent complexes of bivalent nickel, palladium, platinum, and copper, and showed that in the case of these elements there is definite evidence for the frequent occurrence of a planar configuration. Sugden [2] pointed out that there are now three main lines of evidence which lead to this conclusion in the cases of nickel,[3] palladium,[4] and platinum.[5] First, there is the occurrence of *cis–trans*-isomerides when two unsymmetrical chelate groups are attached to the metallic atoms. Examples of this are found in the isomeric nickel derivatives of benzylmethylglyoxime and the isomeric glycine derivatives of palladium and platinum (I) and (II). Secondly, there is the evidence provided by the resolution of a

(I.)





(II.)

4-covalent compound of bivalent platinum. This work of W. H. Mills and T. H. H. Quibell [6] was discussed in the Report last year. Finally, there are the *X*-ray studies by E. G. Cox, W. Wardlaw, and collaborators [7] who, in the last two years, have demonstrated a

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[2] *Nature*, 1936, **137**, 543.

[3] S. Sugden, *J.*, 1932, 246.

[4] F. W. Pinkard, E. Sharratt, W. Wardlaw, and E. G. Cox, *J.*, 1934, 1012.

[5] A. A. Grünberg and B. W. Ptizyn, *J. pr. Chem.*, 1933, [ii], **136**, 143.

[6] *J.*, 1935, 839.

[7] See E. G. Cox, F. W. Pinkard, W. Wardlaw, and K. C. Webster, *J.*, 1935, 459; E. G. Cox, W. Wardlaw, and K. C. Webster, *J.*, 1935, 1475.

planar configuration in no less than 14 derivatives of nickel, palladium, and platinum. Thus there is, in Sugden's view, abundant evidence for planar structures in co-ordination compounds of 4-covalent nickel, palladium, and platinum.

Obviously there must be a theoretical explanation why in certain cases the structure is tetrahedral, and in others planar, and the reader will probably recall that in 1931 L. Pauling [8] put forward a theory to explain this. In connection with this theory it should be noted that the electrons in an octet are divided into two sub-groups of 2 and 6, and those of an 18 group into three sub-groups of 2, 6, and 10. The values of the second quantum number for these sub-groups are $k = 1, 2, 3$, and the spectroscopic designations of the three are *s*, *p*, and *d* respectively. Pauling accepts the idea that a bond involves two electrons, and he lays down that when the links are tetrahedrally distributed these bonds are compounded of electrons in *s* and *p* levels. Generally, it might be said that the links are of the form sp^3. When however one *d* level is used and the links are of the type sp^2d, Pauling predicts an arrangement of four bonds at 90° in one plane. Such vacant *d* levels, with energies comparable with *s* and *p* levels, are found in the atoms of the transition elements. Moreover, since the *d* electrons are chiefly responsible for the magnetic moment of the atom, sharing of them should reduce this property so that bivalent nickel, which is paramagnetic in its simple salts, should become diamagnetic in its 4-covalent planar compounds. It is interesting to find that the recorded magnetic evidence for nickel agrees with Pauling's theory, for all the planar compounds investigated have proved to be diamagnetic. With palladium and platinum, the magnetic evidence does not appear to be so significant, for all simple and complex salts of these elements are diamagnetic, but the diamagnetism of the planar compounds is in accord with Pauling's views. Sugden indicates, however, that a real discrepancy arises with certain cupric compounds. E. G. Cox and K. C. Webster [9] have found from *X*-ray studies that the cupric derivatives of β-diketones have a planar configuration. These compounds are paramagnetic, and there is not a vacant 3 *d* level in the cupric ion. This is readily seen from the electron distributions for nickel and copper atoms, which show that the difference between nickel and copper is not merely the addition of an electron in the nickel atom but a change in the number of electrons in the *d* level :

Ni (At. no. 28) ……	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^8$	$4s^2$
Cu (At. no. 29) ……	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^{10}$	$4s^1$

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[8] *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

[9] *J.*, **1935**, **731.**

The planar configuration for 4-covalent cupric compounds is now firmly established. J. M. Robertson [10] found that in the phthalocyanines of nickel, platinum, and copper the metal atom and the four surrounding nitrogens lie in one plane. Again, an *X*-ray investigation of the crystal structure of cupric chloride dihydrate, $CuCl_2,2H_2O$, by D. Harker,[11] shows that each copper atom is attached to two chlorine and two oxygen atoms by covalent linkings directed to the corners of a square. To illustrate how *X*-ray results can give evidence of this planar structure in simple derivatives of 4-covalent copper, details of a recent investigation [12] of $CuCl_2py_2$ may be given. This substance, which crystallises well from methyl alcohol, was prepared under a variety of experimental conditions with the object of discovering the theoretically possible *cis*- and *trans*-isomerides. Under all conditions it was found to crystallise in the same *trans*-planar form. It is evident that 4-covalent copper compounds of *cis*-configuration, like those of palladium, are generally unstable when chelate groups are absent. That $CuCl_2py_2$ has a *trans*-planar configuration follows from a consideration of its cell dimensions as determined by *X*-ray methods. The short length of the *c* axis (3·84 A.) shows that the pyridine rings must be coplanar (or very nearly so), since this value is of the same order as the distance of approach of $=CH-$ groups in different organic molecules (*ca.* 3·7 A.). Reference to a model shows that this can only be so in a molecule of *trans*-planar configuration (Fig. 2) for with a *cis*-planar configuration the parallel arrangement of the pyridine rings shown in Fig. 1 is impossible on account of the

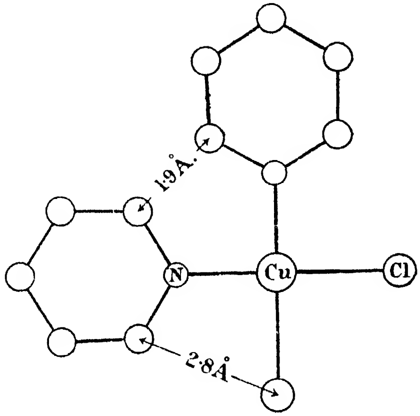

FIG. 1.

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[10] *J.*, 1935, 613.

[11] *Z. Krist.*, 1936, **93**, 136.

[12] E. G. Cox, E. Sharratt, W. Wardlaw, and K. C. Webster, *J.*, 1936, 129.

proximity of the two rings (minimum distance 1·9 A. instead of 3·7 A.). In order to obtain the requisite clearance between the rings in a *cis*-planar structure they must be rotated about the N–Cu bonds through approximately 40°, thus increasing the thickness of the molecule and necessitating a *c*-axis of at least 4·5 A.

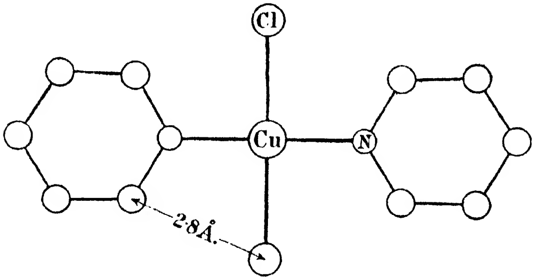
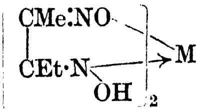


Fig. 2.

This is impossible in view of the experimental datum that *c* is 3·84 A. On the same grounds, a molecule in which the distribution of copper valencies is tetrahedral is excluded. Since the distribution of valencies in nickel and copper 4-covalent compounds may be planar, and the metal atoms are not greatly different in radius, it is to be expected that corresponding nickel and copper compounds will sometimes be isomorphous. This has proved to be the case with the methylethylglyoxime derivatives (III).[12] In view of Sugden's findings [13] that the nickel derivatives of unsymmetrical glyoximes are planar, this result adds additional weight to the conclusion that 4-covalent copper may be planar in its cupric compounds.



$$\left[\begin{array}{l}\text{CMe:NO}\\ |\\ \text{CEt·N}\\ \quad\ \ \text{OH}\end{array}\right]_2 \rightarrow \text{M}$$

(III.)

In a paper on the stereochemistry of the metallic phthalocyanines, R. P. Linstead and J. M. Robertson [14] have shown that bivalent 4-co-ordinate beryllium, manganese, iron, and cobalt, like nickel, copper, and platinum, all exhibit planar symmetry in the crystals of their phthalocyanine derivatives (see Fig. 3). The fact that cobalt is tetrahedral [15] in the group $CoCl_4''$ makes the result with the phthalocyanine derivatives particularly interesting, and provides the first example of this metal exhibiting planar symmetry. The most remarkable of these results, however, is provided by beryllium, for which a tetrahedral symmetry is well established by both chemical and physical considerations. Beryllium is tetrahedral

[13] H. J. Cavell and S. Sugden, *J.*, 1935, 621.

[14] *J.*, 1936, 1736.

[15] H. M. Powell and A. F. Wells, *J.*, 1935, 359.

in its benzoylpyruvic acid derivative [16] and in basic beryllium acetate,[17] and $BaBeF_4$ is isomorphous with $BaSO_4$.[18] That the very simple atom beryllium, which normally contains no *d* electrons, should adopt a planar distribution of valencies, appears inexplicable on Pauling's theory. Linstead and Robertson point out that the theoretical difficulty can be avoided by the assumption that in beryllium phthalocyanine the metal is combined with only two nitrogen atoms, but there seems no justification for arbitrarily differentiating between this compound and the other covalent metallic phthalocyanines which resemble it so closely in crystalline form. The general conclusions from these facts are : (1) that in the metallic phthalocyanines, and probably also the corresponding porphyrins, the rigid planar organic portion of the molecule imposes its steric requirements upon the metal, and (2) that there is more tolerance in the distribution of valencies about 4 co-ordinate-metal atoms than has hitherto been realised.

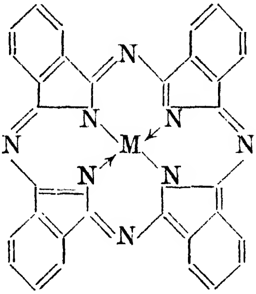


FIG. 3.

The work already surveyed has shown that many 4-covalent complexes of copper, nickel, palladium, and platinum actually possess a planar configuration, and that this configuration is maintained even when considerable changes are made in the nature of the co-ordinate groups. On the other hand there is definite evidence that a change in the principal valency of the metal may lead to a change in the spatial distribution of the bonds. For example, trimethylplatinic chloride, $Pt(CH_3)_3Cl$, in which platinum is 4-covalent but also quadrivalent, has been shown [19] to be non-planar and is most probably tetrahedral. Again, nickel carbonyl, $Ni(CO)_4$,[20] in which the nickel has no principal valency, possesses a

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[16] W. H. Mills and R. A. Gotts, *J.*, 1926, 3121.

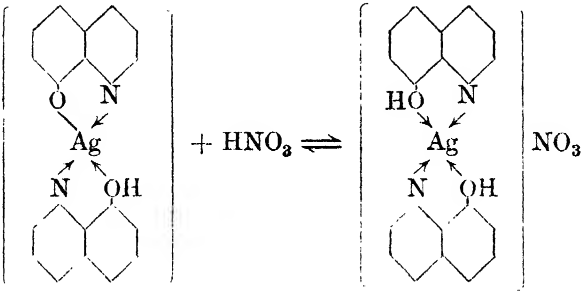
[17] (Sir) W. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437.

[18] N. N. Rây, *Z. anorg. Chem.*, 1931, **201**, 289.

[19] E. G. Cox and K. C. Webster, *Z. Krist.*, 1935, *A*, **90**, 561.

[20] L. O. Brockway and P. C. Cross, *J. Chem. Physics*, 1935, **3**, 828.

tetrahedral structure. Recent investigations have provided additional examples of this change of structure with change in the principal valency of the central element. For instance, in striking contrast to the planar 4-covalent derivatives of bivalent copper, it has been proved that some 4-covalent cuprous compounds are tetrahedral. Similarly, silver has been found to be planar when bivalent and tetrahedral when univalent. Prior to this year, the only evidence on the configuration of either 4-covalent cuprous or argentous derivatives was that of F. Hein and H. Regler, who, in a preliminary note,[21] claimed to have effected a partial resolution of an argentous derivative of 8-hydroxyquinoline. Since then, these authors [22] have described their work in detail, and state that by the use of bromocamphorsulphonate they have obtained evidence that their silver compound is optically active and must therefore have a tetrahedral disposition for the valency bonds of the silver atom. They were unable however to retain the activity when the optically active acid was removed.



E. G. Cox, W. Wardlaw, and K. C. Webster [23] have examined by X-ray methods potassium cuprocyanide, $K_3[Cu(CN)_4]$, and the isomorphous substances tetrakis-thioacetamide cuprous and argentous chlorides [as (IV)]. In each of these substances a tetrahedral valency distribution has been found, and it will be noted that in every case the effective atomic number of the metallic atom is that of an inert gas. It is also noteworthy that the complex ion $Cu(CN)_4'''$ has exactly the same number of electrons, and presumably the same electronic distribution, as the neutral complex $Ni(CO)_4$, which has been shown to be tetrahedral. This tetrahedral distribution of valencies in a co-ordinated cuprous complex has also been found by F. G. Mann, D. Purdie, and A. F. Wells [24] in the molecule $[Et_3As \rightarrow CuI]_4$. Silver, with a principal valency of two

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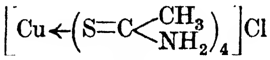
[21] *Naturwiss.*, 1935, **23**, 320.

[22] *Ber.*, 1936, **69**, 1692.

[23] *J.*, 1936, 775.

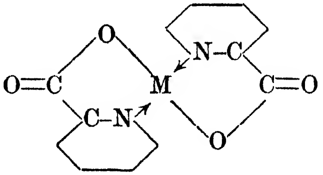
[24] *Ibid.*, p. 1503.

and a covalency of four, has proved [23] to be planar as a result of an *X*-ray examination of the argentic derivative of picolinic acid. This result is based on the high birefringence of the compound and its isomorphism with the corresponding copper derivative, which has been shown to be *trans*-planar as in (V). Further, E. G. Cox and K. C. Webster [25] have demonstrated that potassium auribromide, $K[AuBr_4],2H_2O$, in which gold is tervalent, possesses the ion $AuBr_4'$ with a planar configuration. The *X*-ray evidence shows that the water in the auribromide is held mainly as water of crystallisation, and that the substance does not contain the sexacovalent complex $[AuBr_4,2H_2O]'$. This appears to be the first example of a tervalent metal with a planar distribution for its four valency bonds. It will be realised that a definite advance in the stereochemistry of these so-called currency metals has been made. Some years ago R. Dickinson [26] investigated the complex cyanides of potassium with zinc, cadmium, and mercury of the type $K_2[X(CN)_4]$, and found that the co-ordinated cyanogen groups had a tetrahedral arrangement around the central metal atom. W. H. Mills and R. E. D. Clark [27] have prepared compounds of the type (VI), where M = Hg, Cd, and Zn, in order to investigate the stereochemistry of these metals in the 4-covalent state. Various alkaloid salts were investigated, but in no case could direct evidence of their optical resolution be obtained. Nevertheless, other results of great interest were recorded, but as these cannot be satisfactorily summarised, the original papers must be consulted.

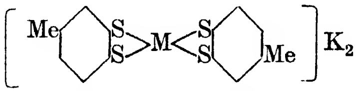


$$\left[Cu \leftarrow \left(S{=}C{<}\begin{matrix}CH_3\\NH_2\end{matrix}\right)_4\right]Cl$$

(IV.)



(V.)



(VI.)

Outside the range of the transition elements, the stereochemistry of 4-covalent tin and lead has been considered. A tetrahedral distribution for the four valencies of stannic tin is firmly established by chemical and physical methods. An optically active compound of tin was prepared by W. J. Pope and S. J. Peachey [28] in 1900, and

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[25] *J.*, 1936, 1635.

[26] *J. Amer. Chem. Soc.*, 1922, **44**, 774.

[27] *J.*, 1936, 175.

[28] *P.*, 1900, **16**, 42, 116.

this tetrahedral configuration was also revealed in the four atoms of iodine which surround the metal in stannic iodide.[29] Until recently, however, no attempt had been made to determine whether this tetrahedral distribution also holds for 4-covalent compounds of stannous tin. The preliminary results of an investigation of $K_2[SnCl_4],2H_2O$ have been published,[30] and they show that in contrast to SnI_4 the complex ion $SnCl_4''$ is planar. The *X*-ray results plainly prove that the tin is 4-covalent, and not sexacovalent as the presence of the two molecules of water might suggest. Other stannous compounds lead to a similar conclusion. Further, lead, which is tetrahedral in the 4-covalent and quadrivalent lead compound, $PbPh_4$,[31] proves to be planar in its bivalent and 4-covalent derivatives such as lead benzoylacetonate, lead salicylate, and $PbCl_2,2CS(NH_2)_2$.[30] This short summary indicates that investigations on 4-covalent compounds are yielding results of considerable interest and value.

Although the structure of compounds of the type AB_5 has not yet been determined, suggestions have been made as to possible configurations. Iron pentacarbonyl, $Fe(CO)_5$, is a substance of this type, and two possible structures have been advocated. The first is a tetragonal pyramid in which the apical carbon monoxide molecule is further removed from the central atom than the other four; such is the structure advanced by W. Graffunder and G. Heymann [32] to explain the small dipole moment. The second, which J. S. Anderson [33] considers more probable, is a trigonal bi-pyramid. It provides the closest packing possible in a 5-covalent arrangement, and affords a satisfactory explanation of the ready formation of $Fe_2(CO)_9$ as formulated by N. V. Sidgwick and R. W. Bailey [34] and described in a previous Report.[35]

Anomalies in the parachor of co-ordination compounds were observed by S. Sugden,[36] who found that beryllium in the basic propionate $Be_4O(C_2H_5{\cdot}CO_2)_6$ and the acetylacetonate appeared to have a variable negative parachor. Co-ordination compounds of thallium and aluminium displayed a similar anomaly, and in last year's Report attention was directed to some results of F. G. Mann and D. Purdie,[37] who found that in certain series of organic metallic

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[29] R. G. Dickinson, *J. Amer. Chem. Soc.*, 1923, **45**, 958.

[30] E. G. Cox, A. J. Shorter, and W. Wardlaw, *Nature*, 1937, **139**, 72.

[31] W. H. George, *Proc. Roy. Soc.*, 1927, *A*, **113**, 585.

[32] *Z. physikal. Chem.*, 1932, *B*, **15**, 377.

[33] *J.*, 1936, 1283.

[34] *Proc. Roy. Soc.*, 1934, *A*, **144**, 521.

[35] *Ann. Reports*, 1934, **31**, 104.

[36] " Parachor and Valency," London, 1930, p. 145.

[37] *J.*, 1935, 1549.

compounds, both simple and complex, the metal atom showed an apparent parachor which fell steadily as the homologous series was ascended. For example, in the homologous series $PdCl_2,2R_2S$ the parachor of palladium fell from 36 for the methyl to − 7 for the *n*-amyl compound. Sugden sought to obviate the anomaly in the compounds of beryllium, thallium, and aluminium by a singlet-link theory of co-ordination; in the case of palladium derivatives, however, the deficit cannot be explained by substituting a singlet linkage for the co-ordinate linkage, but must be regarded as a real effect. Mann and Purdie suggested that the effect might be explained, in part at least, as due to the molecular shape, since the *trans*-planar arrangement of groups about the palladium confers a molecular configuration which might well be associated with anomalous packing effects. This explanation may account in some measure for the results of the parachor in the homologous series considered by Mann and Purdie, but it cannot be regarded as complete in view of some new results by J. S. Anderson [33] on the parachors of metal carbonyl compounds. These compact, non-planar molecules show a large anomaly in their parachors. Nickel carbonyl, which is tetrahedral,[20] and has a close-packed structure, gives a parachor which is a few units greater than four times the observed parachor of carbon monoxide. For iron pentacarbonyl the observed total parachor is less than four times that of carbon monoxide. In the carbonyls the available evidence indicates that the carbon–oxygen linkage differs very little from that in carbon monoxide, so that the assumption that the parachor of co-ordinated CO is the same as that of free carbon monoxide should give an approximate value for the parachor of the metal atom. The parachors of the tricarbonylnitrosylcobalt, $Co(CO)_3(NO)$, and dicarbonyldinitrosyliron, $Fe(CO)_2(NO)_2$, have also been determined. The assumption is made that as NO must be closely related to CO in the nitrosocarbonyls, it is therefore reasonable to calculate the parachor on the relation $P_{NO} - P_{CO} = P_N - P_C$. The parachors of the metals calculated in this way are given in the following table :

	$Ni(CO)_4$.	$Co(CO)_3NO$.	$Fe(CO)_2(NO)_2$.	$Fe(CO)_5$.	CO.
P	255·3	249·8	252·5	300·6	61·6
Apparent P of metal	8·9	−8·9	−18·5	−7·4	

From Sugden's atomic number–parachor curve, iron, cobalt, and nickel should have nearly equal atomic parachors of about 50 (Cr = 54·3, Cu = 46). It is plain that all four substances show a large deficit, just as do the co-ordination compounds of beryllium or palladium. No adequate explanation of this anomaly has yet been advanced.

In the most stable derivatives of cuprous copper the co-ordination number appears to be four, as, *e.g.*, in $K_3[Cu(CN)_4]$. It is interesting to find, therefore, that cuprous and silver iodides form compounds [24] with tertiary phosphines and arsines analogous to the well-known non-ionic aurous chloride derivatives, $R_3P(As)\rightarrow AuCl$, and that many members of this series possess considerable stability in spite of the fact that the metal atom has apparently a co-ordination number of 2. Actually, one would have expected the stable compounds to be of the type $(PR_3)_3CuI$, where copper would have an atomic number of 36 and thereby attain the electronic structure of krypton. *X*-Ray analysis [24] of the arsine compound shows that the true molecule is not $R_3As\rightarrow CuI$, but that it really consists of four simple units $(Et_3As\rightarrow CuI)_4$, and this is in accordance with molecular-weight determinations by the cryoscopic method. The phosphine derivative $Et_3P\rightarrow CuI$ is strictly isomorphous with the triethylarsine compound and has therefore the same structure. The detailed structure shows that the four cuprous atoms are arranged at the apices of a regular tetrahedron and the four iodine atoms lie each at the centre, but above the plane, of one face of the tetrahedron. Beyond each cuprous atom is an arsenic atom lying on the elongation of the axis joining the centre of the tetrahedron to the copper. The three ethyl groups are then joined to each arsenic atom, so that the tetrahedral angle is subtended both at the arsenic and at the first carbon atom of the ethyl groups. The stability is conferred by each iodine atom, in addition to being covalently linked to its original copper atom, also being joined by two co-ordinate links to the other two copper atoms of the same tetrahedral face. Each copper atom acquires seven electrons and is identical, therefore, in both co-ordination number and electronic structure, with that in $K_3[Cu(CN)_4]$.

Benzoinoxime, as is well known, is one of a number of organic reagents employed in the detection and estimation of metals. The copper derivative, discovered by F. Feigl,[38] is a deep green amorphous compound, insoluble in water and organic solvents, to which formula (VII) was assigned. Until recently, however, this structure could not be regarded as fully established. It is unusual to find the hydrogen atom of the secondary alcoholic group replaced by copper; moreover, benzoinoxime is a reducing agent, and one would expect it to reduce a proportion of the cupric salt to the cuprous state. From the analytical data, structure (VIII), which is that of a cuprous compound, is a possible alternative to (VII). Convincing evidence that the structure is (VII) has been obtained by treating Feigl's compound with alcoholic hydrogen chloride. A

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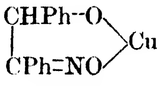
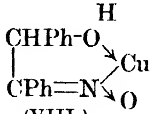
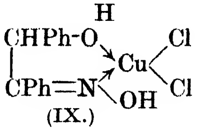
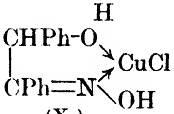
[38] *Ber.*, 1923, **56**, 2083.

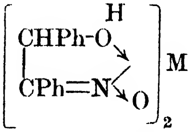
green crystalline salt (IX) then separates with a molecule of alcohol of crystallisation. With hot water, two molecules of hydrogen chloride are eliminated from (IX) and the original compound (VII) is produced. A compound of formula (VIII) on treatment with alcoholic hydrogen chloride would give the derivative (X). Whilst Feigl's compound must therefore have structure (VII), there is, at present, no direct evidence whether the ring is five- or six-membered. It has also been shown [39] that nickel, palladium, and platinum give covalent compounds of the type (XI), where M = Ni, Pd, or Pt, and it has also been demonstrated that in the case of nickel the oxime may function as a chelate group attached by two co-ordinate links. It will therefore be seen that benzoinoxime forms co-ordination compounds with a number of metals and can act as a chelate group in three ways. In Feigl's compound it may be attached to a copper atom by two principal valencies; with other bivalent metals it may be associated either by one principal valency and one co-ordinate link as in (XI), or by two co-ordinate links.


(VII.)

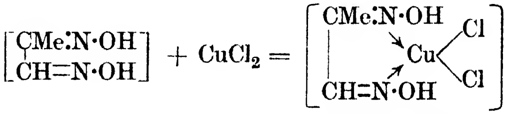

(VIII.)


(IX.)

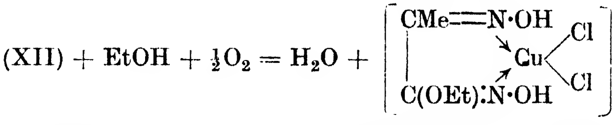

(X.)


(XI.)

When anhydrous cupric chloride reacts with a glyoxime, such as dimethyl- or benzylmethyl-glyoxime, in ethyl-alcoholic solution, green crystalline co-ordination compounds (XII) are produced of a type different from the more familiar nickel derivatives. In these copper compounds the oxime is functioning as a chelate group attached by two co-ordinate links. When methylglyoxime is employed, not only is a co-ordination compound of type (XII) obtained, but a second product of entirely different constitution


(XII.)

$$\begin{bmatrix} \text{CMe:N·OH} \\ \text{CH=N·OH} \end{bmatrix} + \text{CuCl}_2 = \begin{bmatrix} \text{CMe:N·OH} \to \text{Cu}\text{Cl}_2 \leftarrow \text{CH=N·OH} \end{bmatrix}$$


(XIII.)

$$(\text{XII}) + \text{EtOH} + \tfrac{1}{2}\text{O}_2 = \text{H}_2\text{O} + \begin{bmatrix} \text{CMe=N·OH} \to \text{Cu}\text{Cl}_2 \leftarrow \text{C(OEt):N·OH} \end{bmatrix}$$

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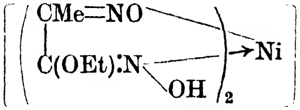
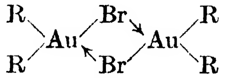
[39] J. S. Jennings, E. Sharratt, and W. Wardlaw, *J.*, 1935, 818.

(XIII) may be produced. A new chelate group is formed[40] in the reaction. This methylalkoxyglyoxime may readily be distinguished from the familiar dialkylglyoximes by the colour of its nickel derivative. For example, the dimethylglyoxime of nickel is crimson, but the methylethoxyglyoxime (XIV) is orange.

Although gold may be tervalent, there is no evidence that a tervalent gold ion can exist. However, when suitably co-ordinated, this metal can form part of a tervalent cation as in $(\mathrm{Au\,en_2})\mathrm{Br_3}$, where gold has a covalency of four.[41] This covalency of four is also exhibited in the dialkyl compounds of tervalent gold, which have been shown to have the symmetrical constitution (XV),

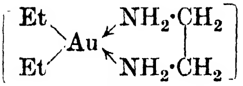
(XIV.)



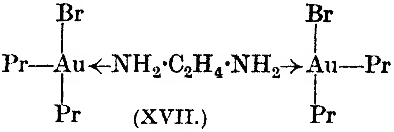


(XV.)

and tribromogold is similarly formulated.[42] When these dialkyl compounds are treated with ethylenediamine there is an interesting difference between the behaviour of the diethyl and the di-*n*-propyl derivative. Diethylbromogold[43] yields directly the co-ordination compound (XVI), but the di-*n*-propyl compound[44] gives the intermediate derivative (XVII), which in chloroform slowly yields a mixture of the original di-*n*-propylbromogold and the di-*n*-propyl analogue of (XVI). When diethyl- or di-*n*-propyl-bromogold is



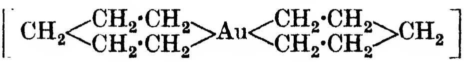
(XVI.)



$$\mathrm{Pr{-}\overset{\displaystyle Br}{\underset{\displaystyle Pr}{Au}}{\leftarrow}NH_2{\cdot}C_2H_4{\cdot}NH_2{\rightarrow}\overset{\displaystyle Br}{\underset{\displaystyle Pr}{Au}}{-}Pr}$$

(XVII.)

heated with silver cyanide,[45] the corresponding cyano-compound is obtained as a colourless crystalline non-electrolyte which proves to be tetrameric in freezing bromoform. Reactions with ethylenediamine lead to crystalline salts $\mathrm{R_2Au{\cdot}CN{\cdot}en{\cdot}CN{\cdot}AuR_2}$. In the Report for 1933 it was stated that C. S. Gibson[46] had announced the preparation of two auric derivatives of unusual type (XVIII)



$$\left[\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{Au}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH_2}\right]\mathrm{Br}$$

(XVIII.)

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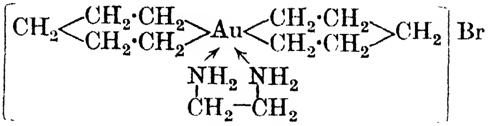
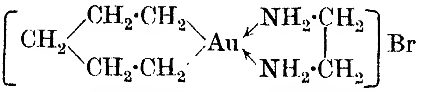
[40] E. Sharratt and W. Wardlaw, *J.*, 1936, 563.
[41] C. S. Gibson and W. M. Colles, *J.*, 1931, 2410.
[42] A. Burawoy and C. S. Gibson, *J.*, 1935, 217.
[43] C. S. Gibson and J. L. Simonsen, *J.*, 1930, 2531.
[44] A. Burawoy and C. S. Gibson, *J.*, 1935, 219.
[45] A. Burawoy, C. S. Gibson, and S. Holt, *ibid.*, p. 1024.
[46] *Nature*, 1933, **131**, 130.

and (XIX). He now states[47] that in the light of further experimental work the constitutions of these compounds must be corrected to (XX) and (XXI) respectively.

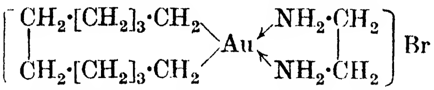
(XIX.)



(XX.)



(XXI.)



It will be recalled that a few years ago H. Carlsohn,[48] by a simple but ingenious reaction, prepared a nitrate of iodine, co-ordinated with one or two molecules of pyridine. A solution of iodine in chloroform was added to silver nitrate dissolved in a chloroform–pyridine mixture; silver iodide was precipitated and dipyridine iodine nitrate $INO_3,2py$ crystallised from the filtrate. A molecule of pyridine was lost when the compound was left in a desiccator over sulphuric acid. More recently,[49] the bromine analogue has been prepared by a similar method. H. Carlsohn obtained it as a hygroscopic substance by adding bromine in chloroform to silver nitrate in a chloroform–pyridine mixture, removing the silver bromide, and adding the filtrate to ether containing a little pyridine. A dipyridine bromine perchlorate has also been isolated. Apparently co-ordination with pyridine is necessary for the isolation of these interesting substances.

The fundamental principles of Werner's theory are now so firmly established that it can be asserted with confidence that when a substance is formulated at variance with these principles then the formulation is incorrect. In the course of his researches on ruthenium, A. Joly[50] prepared its trichloride, $RuCl_3$, and noted that it would absorb ammonia with the formation of an ammine, which was stated to be $Ru_2Cl_6,7NH_3$. By the action of water it yielded an intense violet-red solution from which was obtained a crystalline hydroxy-compound, to which the formula $Ru_2Cl_4(OH)_2,7NH_3,3H_2O$ was assigned. This hydroxy-compound, also obtained by the action

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[47] *J.*, 1936, 324.

[48] Habilitat. Schrift., 1932 (S. Hirzel, Leipzig).

[49] M. I. Uschakov and V. O. Tchistov, *Ber.*, 1935, **68**, 824; H. Carlsohn, *ibid.*, p. 2209.

[50] *Compt. rend.*, 1892, **114**, 291; **115**, 1299.

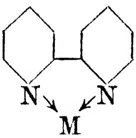
of ruthenium trichloride on aqueous ammonia, is known as "ruthenium red" and dyes animal fibres in red shades. Both formulæ seem unlikely in the light of modern ideas on molecular structure, and an investigation by G. T. Morgan and F. H. Burstall [51] has shown that the $Ru_2Cl_6,7NH_3$ is not a simple substance but a mixture of amminated chlorides, probably including the hexammine $[Ru(NH_3)_6]Cl_3$. Moreover, "ruthenium red" proves to be the co-ordination compound $[Ru(OH)Cl(NH_3)_4]Cl,H_2O$, in which ruthenium has the usual co-ordination number six. With hydrochloric acid it gives the yellow salt $[RuCl_2(NH_3)_4]Cl,2H_2O$. It is interesting to find that when the ammonia molecules are replaced by ethylenediamine, ethylamine, or pyridine, the tinctorial power is greatly reduced. Morgan and Burstall suggest that a possible explanation lies in the fact that ammonia may induce a different distribution of the hydroxy- and chloro-groups from that of these other ammines. It is obvious in the octahedral arrangement shown by "ruthenium red" and its analogues that the hydroxy- and chloro-groups may occupy *cis*- or *trans*-positions relative to one another. F. H. Burstall [52] has recently described a series of very stable red co-ordination compounds $[Ru\ 3dipy]X_2,yH_2O$ which have been obtained by the action of 2 : 2′-dipyridyl on ruthenium salts. By the interaction of this diamine and ruthenium trichloride at 250°, an almost quantitative yield of the complex chloride

$$[Ru\ 3dipy]Cl_2,6H_2O$$

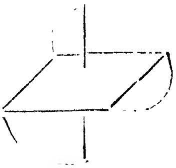
may be isolated from the reaction products :

$$2RuCl_3 + 8C_{10}H_8N_2 = 2[Ru\ 3dipy]Cl_2 + C_{20}H_{14}N_4 + 2HCl$$

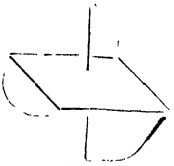
The stability of these tris-2 : 2′-dipyridylruthenous salts is remarkable; they can be boiled with concentrated (50%) potassium hydroxide solution without destruction of the complex cation. As the base, dipyridyl, forms a chelate ring in the same way as ethylenediamine [cf. (I)], these trisdipyridylruthenous salts should be capable of resolution. With the aid of *d*- and *l*-ammonium tartrates, the complex [Ru 3dipy] has been resolved into optically active forms (II) and (III), and the optically active bromides isolated. These



(I.)



(II.)



(III.)

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[51] *J.*, 1936, 41.

[52] *Ibid.*, p. 173.

gave $[\alpha]^{25°}_{5791}$ + 860° and — 815°. In 1931 R. Charonnat[53] obtained *d*- and *l*-forms of the complex salt $R[Ru(NO)(C_5H_5N)(C_2O_4)_2]$, where R is NH_4 or C_5H_6N. Here the ruthenium is present as a complex anion. H. Gleu and K. Rehm[54] record that they have obtained luteo- and purpureo-salts of ruthenium. The former are the stable hexammines, $[Ru(NH_3)_6]_2(SO_4)_3,5H_2O$ and

$$[Ru(NH_3)_6]H(SO_4)_2,$$

and the latter are the pentammines $[Ru(NH_3)_5Br]Br_2$ and

$$[Ru(NH_3)_5Cl]Cl_2.$$

These compounds are analogous with the corresponding well-known cobalt and chromium ammines, but the hexammines of ruthenium are colourless like those of rhodium. All the compounds are paramagnetic, with a moment of 2 Bohr magnetons at 20°.

The heats of formation and solution of some isomeric cobaltammines have been determined by T. C. J. Ovenston and H. Terrey.[55] The method adopted was to decompose the ammine with an excess of *M*-sodium sulphide. The reaction can be represented for the tetrammine salts by the equation

$$2[Co(NH_3)_4Cl_2]\,Cl + 3Na_2S = Co_2S_3 + 8NH_3 + 6NaCl + 2Q \text{ cals.}$$

If the heats of formation, in solution, of sodium sulphide and chloride and ammonia (or other amine) and the heat of formation of solid cobaltic sulphide are substituted in the equation, then the required heat of formation can be calculated from *Q*. The results are summarised below :

	Heat of formation, cals.	Heat of solution, cals.
trans-$[Co(NH_3)_4Cl_2]Cl$	214,800	−8290
cis- ,, ,, ...	214,170	−9510
trans-[Co en_2Cl_2]Cl	171,920	−5340
cis- ,, ,, ...	172,830	−8010

Although much work has been done on the vapour tensions of ammines, mention should be made of a very interesting series of results obtained by G. Spacu and P. Voichescu.[56] In a study of certain ammoniates of the thiocyanate, formate, acetate, chromate, glycollate and other salts of the ion Cu^{2+}, the strength of the bond between the metal ion and ammonia was found to be inversely proportional to the base strength of the anion of the salt, under otherwise comparable conditions.

In his papers reporting the discovery of unusually stable com-

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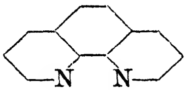
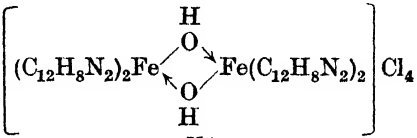
[53] *Ann. Chim.*, 1931, **16**, 126.
[54] *Z. anorg. Chem.*, 1936, **227**, 237.
[55] *J.*, 1936, 1660.
[56] *Z. anorg. Chem.*, 1936, **226**, 273.

plexes with *o*-phenanthroline (IV), F. Blau [57] draws attention to the existence of two different ferric complexes. The blue one is obtained only by oxidation of the ferrous complex whose formulation is well established as $[Fe(C_{12}H_8N_2)_3]^{2+}$; analysis of its chloroplatinate showed it to be $[Fe(C_{12}H_8N_2)_3]^{3+}$. By contrast, direct reaction of *o*-phenanthroline and ferric salts led to the formation of brown solutions from which Blau isolated no solid compounds. A. Gaines, L. P. Hammett, and G. H. Walden [58] have now obtained from these brown solutions an interesting crystalline salt of definite composition whose properties correspond to the formula of a tetraphenanthroline-dioldiferric chloride (V). The iron atoms have a covalency of 6



(IV.)



$$\left[(C_{12}H_8N_2)_2Fe\genfrac{}{}{0pt}{}{\overset{H}{O}}{\underset{H}{O}}Fe(C_{12}H_8N_2)_2\right]Cl_4$$

(V.)

and the unusually low magnetic susceptibility of the new complex suggests the partial neutralisation of the magnetic moments of the two atoms, and is additional evidence of a polynuclear structure. There is nothing repugnant in this formulation. The ease of formation and stability of the double " ol " bridge are well established for cobaltic and chromic ammines and are basic features of the theories of colloidal oxides which E. Steasni [59] and A. W. Thomas [60] have developed.

Many facts have come to light from a study of the rotatory power of complex inorganic compounds, with a covalency of six. Studies of such compounds have been made by F. M. Jaeger,[61] J. Lifschitz,[62] C. H. Johnson,[63] R. Samuel,[64] and many others. A. Werner,[65] it will be remembered, carried out many transformations involving optically active compounds in his efforts to find a relationship between configuration and direction of rotation. Typical of these investigations are the following:

$$l\text{-}[Co\,en_2Cl_2]Cl + K_2CO_3 \rightarrow d\text{-}[Co\,en_2CO_3]Cl + 2KCl$$
$$l\text{-}[Co\,en_2Cl(SCN)]Cl + NaNO_2 \rightarrow d\text{-}[Co\,en_2(NO_2)(SCN)]Cl + NaCl$$
$$l\text{-}[Co\,en_2Cl(NO_2)]Cl + KCNS \rightarrow l\text{-}[Co\,en_2(NO_2)SCN]Cl + KCl$$

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[57] *Monatsh.*, 1898, **19**, 647.

[58] *J. Amer. Chem. Soc.*, 1936, **58**, 1668.

[59] *Collegium*, 1932, No. 751, 902.

[60] *J. Amer. Chem. Soc.*, 1934, **56**, 794.

[61] "Optical Activity and High Temperature Measurements," New York, 1930.

[62] *Z. physikal. Chem.*, 1923, **105**, 27; 1925, **114**, 485; *Rec. trav. chim.*, 1922, [iv], **41**, 13.

[63] *Trans. Faraday Soc.*, 1932, **28**, 845; 1933, **29**, 626.

[64] *Ibid.*, 1935, **31**, 423.

[65] *Ber.*, 1912, **45**, 1228.

He assumed that no change in configuration took place during these reactions and formulated the structures in accordance with this assumption. The complex salts [Co $en_2Cl(SCN)$]Cl, [Co $en_2Cl(NO_2)$]Cl, and [Co $en_2(NO_2)(SCN)$]Cl were then resolved as bromocamphorsulphonates. Werner now assumed that the complex ions of the same configuration form, in each case, the less soluble salt with the active acid. The experimental results obtained agreed with those based on his first assumption, for the *l*-[Co $en_2Cl(SCN)]^+$,

d-[Co $en_2Cl(NO_2)]^+$,

and *d*-[Co $en_2(NO_2)(SCN)]^+$ ions crystallised as bromocamphorsulphonates in the first fractions. Werner's views have been criticised by F. M. Jaeger,[66] who states that these rules are quite illusory and that a much better criterion of analogous spatial configurations is based on a comparison of the crystal form. J. P. Mathieu,[67] on the other hand, from studies of the optical absorption and rotation of many optically active complex salts, finds some support for Werner's rule relating configuration and solubility of the diastereoisomerides. W. Kuhn and K. Bein [68] have deduced absolute configurations of inorganic compounds from the theory of the origin of optical rotation. J. C. Bailar and R. W. Auten [69] have recently shown that Werner's assumption that atoms or groups in the complex ion are always displaced by others without change of configuration cannot be maintained. They proved that when silver carbonate reacts with *l*-[Co en_2Cl_2]Cl it gives *l*-[Co en_2CO_3]Cl, whereas potassium carbonate gives the dextrorotatory product. A more recent study [70] has demonstrated that an excess of silver carbonate gives the lævo- and a deficiency the dextro-rotatory salt. Potassium carbonate always gives a dextrorotatory product. Of the mechanisms suggested for the Walden inversion, on the basis of the reactions of organic molecules, is one [71] which states that inversion accompanies every reaction. This means that every reaction which involves a single step in the substitution of one group by another on a tetrahedral atom should lead to inversion. Accordingly if the over-all reaction takes place in an odd number of steps the product should be the enantiomorph of the original material. The object of some recent work by J. C. Bailar, J. H. Haslam, and E. M. Jones [72] was to see if this theory might be applied to 6-covalent

[66] Ref. 61, pp. 93, 139.

[67] *Compt. rend.*, 1934, **199**, 278; 1935, **201**, 1183.

[68] *Z. anorg. Chem.*, 1934, **216**, 321.

[69] *J. Amer. Chem. Soc.*, 1934, **56**, 774.

[70] J. C. Bailar, F. G. Jonelis, and E. H. Huffman, *ibid.*, 1936, **58**, 2224.

[71] A. R. Olson, *J. Chem. Physics*, 1933, **1**, 418; E. Bergmann, M. Polanyi, and A. Szabo, *Z. physikal. Chem.*, 1933, *B*, **20**, 161.

[72] *J. Amer. Chem. Soc.*, 1936, **58**, 2226.

inorganic compounds. The case selected was the reaction of ammonia with *l*-[Co en_2Cl_2]Cl. At − 77° or − 33° with liquid ammonia, the product was *l*-[Co $en_2(NH_3)_2$]Cl_3, but at 25° and higher it was the *d*-form. These investigators argue that the two chlorine atoms in the complex ion must be attached to the cobalt atom in exactly the same way, and occupy like positions in the molecule. They assume, therefore, that the same mechanism functions in their displacement from the complex. If this is correct, then the conversion of the dichloro-salt into the diammino-derivative must take place in an even number of steps, and the theory mentioned would allow no inversion. Actually, the reaction does lead to an inversion, for the product at low temperatures is lævo- and that at higher temperatures is dextro-rotatory. The authors [72] point out, however, that it is possible for the displacement in the complex of a chlorine atom by a molecule of ammonia to produce such a profound change in the complex ion that the second step of the reaction does not follow the same mechanism. E. Bergmann [72a] has recently stated that the theory mentioned above [71] is concerned expressly with substitutions of ions for polar bonds and the reaction studied by Bailar is not of this type.

R. Tsuchida, M. Kobayashi, and A. Nakamura [73] have reported that when solutions of certain racemic complex compounds are shaken with powdered quartz, it preferentially adsorbs one antipode, compounds of the same configuration being preferentially adsorbed by quartz of a given sign of rotation. As an example, when a solution of chloroamminobisdimethylglyoxime cobalt [Co$(dm)_2Cl(NH_3)$], Hdm being dimethylglyoxime, is shaken with the quartz powder the supernatant liquid is optically active. This method, it is claimed, may be used to determine whether a given compound is *cis*- or *trans*-. In the case just cited, the complex compound must be of *cis*-configuration, for the *trans*- would be incapable of resolution. Y. Shibata [74] and his colleagues have studied the catalytic oxidation of certain racemic amino-acids in the presence of optically active complex compounds, and state that one isomeride of the amino-acid is oxidised faster than the other. They explain this as being due to an " enzyme-like action " of the inorganic complex. J. C. Bailar [75] suggests as an alternative explanation that one form of the amino-acid becomes part of the complex while the other does not,

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[72a] *J. Amer. Chem. Soc.*, 1937, **59**, 423.

[73] *J. Chem. Soc. Japan*, 1935, **56**, 1339; *Bull. Chem. Soc. Japan*, 1936, **11**, 38.

[74] Y. Shibata and R. Tsuchida, *ibid.*, 1929, **4**, 142; Y. Shibata, Y. Tanaka, and S. Goda, *ibid.*, 1931, **6**, 210.

[75] *Chem. Reviews*, 1936, **19**, 82.

and subsequent oxidation might destroy one or the other. C. E. M. Pugh's results [76] are not in entire accord with those of Shibata.

An interesting account by N. F. Hall [77] of the acid–base properties of complex ions has appeared. He summarises the results on the acid strength of various ammino-cations from the work of Lamb, Werner, and Brönsted. As would be expected, those cations with the greatest tendency to liberate ammonia should be the weakest acids, and this is, in general, the case. It is also interesting to notice from Werner's work [78] on 6-covalent-metal cations that the central atom confers acid strength in the diminishing order

$$Pt^{4+}, Ru^{4+}, Cr^{3+}, Co^{3+}.$$

In connection with complex anions, A. Hantzsch remarked that among the oxygen acids those with the most oxygen were in general the strongest, and that, as a rule, complex anions tend to be weak bases. In two recent papers, I. M. Kolthoff and W. J. Tomsicek [79] have brought forward the striking fact that, although $[Fe(CN)_6]^{3-}$ and $[Mo(CN)_8]^{4-}$ are weak bases, yet $[Fe(CN)_6]^{4-}$ is about as strong a base as the benzoate ion.

An important extension to the chemistry of the metal carbonyls has been made by W. Manchot and W. J. Manchot.[80] They have isolated $Ru(CO)_5$ as a very volatile crystalline compound (m. p. — 22°) by the action of carbon monoxide on finely divided ruthenium at 180° and a pressure of 200 atmospheres. Moreover, by the action of light, or better, by heating its benzene solution, they have prepared from the pentacarbonyl another derivative, $Ru_2(CO)_9$, as orange-yellow crystals which in the absence of air only decompose at 200°. By the action of the halogens on this enneacarbonyl, they have formed compounds of the type $RuX_2(CO)_2$ and have also obtained a nitrosyl compound, $Ru(NO)_4$ or $Ru(NO)_5$, from the interaction of nitric oxide and $Ru_2(CO)_9$. These results emphasise the periodic relationship which is found between iron and ruthenium. The three carbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been the subject of an extensive investigation by W. Hieber, E. Romberg, and F. Mühlbauer.[81] These carbonyls prove to be isomorphous, all forming colourless, strongly refracting, volatile, orthorhombic crystals, readily soluble in inert organic solvents. Compared with other metal carbonyls they are very stable, the vapour decomposing slowly only above 120°. The boiling points (abs./1 atm.) are $Cr(CO)_6$

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[76] *Biochem. J.*, 1933, **27**, 480.

[77] *Chem. Reviews*, 1936, **19**, 89.

[78] " New Ideas on Inorganic Chemistry," London, 1911, p. 201.

[79] *J. Physical Chem.*, 1935, **39**, 945.

[80] *Z. anorg. Chem.*, 1936, **226**, 385.

[81] *Ibid.*, 1935, **221**, 321, 332, 337, 349.

420·5°, $Mo(CO)_6$ 429·4°, $W(CO)_6$ 448·0°. As in the cases of the nickel, cobalt, and iron carbonyls, it is possible to replace the co-ordinated CO group by suitable organic units. For example, by the use of pyridine, the derivatives $Cr(CO)_3$ 3py, $Mo(CO)_3$ 3py, and $W(CO)_3$ 3py have been prepared. Derivatives of similar type have been obtained by the use of such chelate groups as ethylenediamine, *o*-phenanthroline, or αα′-dipyridyl.

There is no doubt that at present most chemists consider that the electron-pair theory of the co-ordinate link offers the best explanation of the many properties of co-ordination compounds. The formation of complex compounds of the olefins with metallic salts supplies an interesting test of the application of the lone-pair bond theory. The first compound of this series was obtained in 1831 by Zeise,[82] who isolated a substance with the empirical formula $K[PtCl_3,C_2H_4],H_2O$ from a reaction mixture of chloroplatinic acid and alcohol. Later, K. Birnbaum [83] prepared similar compounds with propylene and amylene, and C. Chojnacdki [84] obtained $K[PtBr_3,C_2H_4]$. This series of substances is obviously derived from a platinous derivative of the general type PtX_2Y, where X is a halogen atom and Y a molecule of a hydrocarbon. Substances of this type are bimolecular, but it seems most unlikely that Zeise's salt is other than unimolecular, for it has the covalency of 4 which is normally associated with bivalent platinum. Now if the ethylene molecule is associated in the usual way with the central metal atom, a "lone pair" of electrons must be available. These are not apparent in the usual formulation for ethylene and allied molecules. One possible mechanism [85] supposes that the lone pair is produced by an electromeric change, $\mathrm{R{\cdot}CH{=}\overset{\searrow}{C}HR \quad R{\cdot}\overset{+}{C}H{-}\overset{-}{C}HR}$. This involves (*a*) an opening of the double bond, and (*b*) leaving one of the carbon atoms—that which bears the residual positive charge—with a sextet of electrons. Discussing this possibility in the formation of $K[PtCl_3,C_2H_4]$, J. S. Anderson [86] states that it is not altogether free from objection on physical grounds. The hypothetical polarised state of the bond concerned, supposing as it does the complete transfer of one electron, represents an excited state of the molecule and could be represented at room temperature by only a very low probability of occurrence. Alternatively, it might be supposed that rearrangement takes place in the field of the adjacent platinum atom which possesses a high electron affinity. In either

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[82] *Pogg. Ann.*, 1831, **21**, 497.

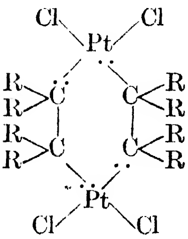
[83] *Annalen*, 1868, **145**, 67.

[84] *Jahresber.*, 1870, **23**, 510.

[85] G. M. Bennett and G. H. Willis, *J.*, 1929, 256.

[86] *J.*, **1936, 1042.**

case the reactions concerned should involve a high energy of activation. There are no data available as to the energy of activation either for the reactions of the type involving formation of complex compounds of olefins with metallic salts or for addition-compound formation by aromatic hydrocarbons, but reactions of both kinds proceed either very rapidly or fairly rapidly at room temperature. Anderson concludes that, on the evidence so far available, any attempt to formulate compounds such as Zeise's salt in terms of the electron-pair bond theory possesses a certain artificiality. T. A. Ashford and M. S. Kharasch[87] have proposed for compounds of the type $PtCl_2,C_2H_4$ a structure which embodies the idea of the electron-pair bond but appears to imply a change in the valency of the platinum from two to four. This is difficult to reconcile with their statement that it is well established that these compounds are derivatives of platinous platinum. It should be mentioned that R. F. Hunter and R. Samuel[88] believe that the conception of the lone pair of electrons as an agent for true chemical linkage is in direct contradiction to the results of band spectroscopy.



Much work of value has been omitted from this report owing to limitations of space, but the Reporter has attempted to deal with a variety of topics in the hope that this course will make the report of wider interest.

W. W.

5. THE RARE EARTHS.

As a general rule, chemists now recognise that the elements of the rare earths are not a confused collection of metals but substances of the highest scientific interest. It is, of course, quite true that there are members of the group so scarce and so difficult to separate that they are little more than names in the list of known chemical elements. Nevertheless, it is not always realised that the group as a whole is as plentiful in nature as lead, zinc, or cobalt, and that cerium, the most abundant member, is more plentiful than silver, gold, or platinum. The following table[1] gives the estimated occurrence of the elements in the earth's crust :

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
At. No.	57	58	59	60	62	63	64	65	66	67	68	69	70	71
$\% \times 10^5$	7	31	5	18	7	0·2	7	1	7	1·2	6	1	7	1·5

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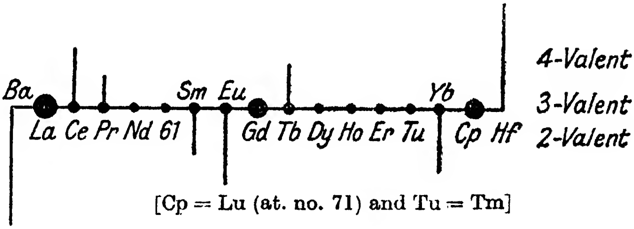
[87] *J. Amer. Chem. Soc.*, 1936, **58**, 1733.

[88] *Nature*, 1936, **138**, 411.

[1] V. M. Goldschmidt and L. Thomassen, *Videnskaps.-Skrifter*, I, *Matemat.-Naturv. Klasse* (*Kristiania*), 1924, No. 5, p. 49.

It shows that the elements of even atomic number are always more abundant than their neighbours of odd atomic number, and this suggests that their stability is closely related to their detailed atomic structures.

At one time the metals of the rare earths were supposed to have an invariable valency of three, so that cerium, being quadrivalent, was considered an intruder. Although it is still correct to say that the characteristic valency of the group is three, yet it is now firmly established that both higher and lower valencies are possible. For instance, cerium, praseodymium, and terbium can be quadrivalent, and samarium, europium, and ytterbium may be induced to show a valency of two. G. Jantsch and W. Klemm,[2] prominent workers on these anomalous valencies, have published a diagram which shows the results of recent investigations. In this diagram (see figure) lines above the central horizontal line represent quadrivalency, and lines below show bivalency. The length of the line gives an approximate measure of the stability, and the size of the point denotes the relative stability of the electronic configuration of the Me^{3+} ion. There is evidence in the cases of lanthanum, gadolinium, thulium, and lutecium that the lower-valency compounds exist, but these have not yet been obtained in a form capable of detailed study. Lanthanum was stated [3] to form an oxide of the quadrivalent element, but this could not be confirmed by G. Jantsch and E. Wiesenberger.[4]



[Cp = Lu (at. no. 71) and Tu = Tm]

These variable valencies are proving most useful in making possible new methods of separation. Cerium, for example, has long been separated from its neighbours by boiling an oxidised solution containing them, whereby ceric salts are readily hydrolysed and precipitated as basic compounds. The new processes, however, utilise a valuable observation first made by Jantsch and his collaborators,[5] that when the rare-earth metals become bivalent,

[2] *Z. anorg. Chem.*, 1933, **216**, 80.

[3] I. M. Kolthoff and R. Elmquist, *J. Amer. Chem. Soc.*, 1931, **53**, 1230.

[4] *Monatsh.*, 1932, **60**, 1.

[5] G. Jantsch, H. Alber, and H. Grubitsch, *Monatsh.*, 1929, **53–54**, 305.

the solubilities of their sulphates resemble those of barium and strontium.

This fact led L. F. Yntema [6] to explore the possibility of separating europium from other rare earths by electrolytic reduction in the presence of the sulphate ion. He dissolved a mixture of the oxides of samarium, europium, and gadolinium in hydrochloric acid, added a small amount of dilute sulphuric acid, and electrolysed this solution in a two-compartment cell with a mercury cathode and platinum anode. As the electrolysis proceeded, colourless europous sulphate, $EuSO_4$, separated. A spectrographic examination of this material showed only a trace of samarium. This method successfully accomplishes one of the most difficult separations in the field of analytical chemistry. A. Brühl [7] states that if the material contains less than 2% Eu_2O_3 there is a greater difficulty in effecting a separation, but co-precipitation with the isomorphous strontium sulphate is helpful. He confirms that the electrolytic method gives good yields of europous sulphate of high purity. R. W. Bell and L. F. Yntema [8] have shown that bivalent ytterbium sulphate may similarly be precipitated from an acid solution by electrolytic reduction in the presence of the sulphate ion. In this way ytterbium may be separated from yttrium, erbium, and thulium. The precipitate has the variable composition $YbSO_4,xH_2O$ and is a very light green crystalline compound. W. Prandtl [9] has used this method to prepare pure ytterbium, but states that it is not always successful. D. W. Pearce,[10] however, has found it satisfactory for the separation of ytterbium from thulium and from lutecium fractions. H. N. McCoy [11] has shown that reduction by zinc, in a modified Jones reductor, changes $EuCl_3$ into the dichloride. Investigators [9, 11] on the sulphates of ytterbium have all commented on the reaction of the yellowish-green $YbSO_4$ with the dilute acid as soon as the current is stopped:

$$2YbSO_4 + 2H^{\cdot} = 2Yb^{\cdot\cdot\cdot} + 2SO_4'' + H_2$$

It appears that the order of decreasing stability amongst the sulphates of the bivalent rare-earth metals is europium, ytterbium, samarium.

During recent years several attempts have been made to evolve methods of separation depending on partial thermal decomposition of rare-earth metal sulphates. For example, H. H. Willard and

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[6] *J. Amer. Chem. Soc.*, 1930, **52**, 2782.
[7] *Angew. Chem.*, 1936, **49**, 159.
[8] *J. Amer. Chem. Soc.*, 1930, **52**, 4264.
[9] *Z. anorg. Chem.*, 1932, **209**, 13.
[10] Thesis, Illinois, 1934.
[11] *J. Amer. Chem. Soc.*, 1936, **58**, 1577.

R. D. Fowler[12] determined the products formed in such decompositions and also the dissociation pressures of the pure anhydrous sulphates at definite temperatures. They then attempted to maintain the partial pressure of sulphur trioxide above the heated isomorphous sulphates at a value intermediate between those of the constituents, and thus bring about complete decomposition of one compound to the insoluble oxide without affecting the others. By adopting these principles, a separation of cerium from other earths was achieved. Cerous sulphate ignited readily to ceric oxide, whilst the associated rare-earth metals remained as the sulphates. It was found that the separation of praseodymium from lanthanum was not completely successful, because the sulphate of the former ignited only partially to the higher-valency oxide, and the success of the separation requires the formation of this higher oxide of praseodymium. Similar work has been carried out recently by L. Wöhler and K. Flick.[13] Attempts to separate rare earths which did not oxidise on ignition were unsuccessful, because the decomposition products formed solid solutions with no appreciable solubility differences between the constituents. D. W. Pearce[14] mentions that he and Kalischer have determined the temperatures at which certain nitrates of the rare-earth metals lose some or all of their water of crystallisation. When certain mixtures of carefully heated, partly dehydrated nitrates are extracted with anhydrous ether at low temperatures separations are obtained.

The magnetic susceptibilities of the rare-earth metals, with anomalous valencies, afford an interesting approach to the study of the electronic structures of the rare-earth metal ions. The large paramagnetism of these metals and their salts is well known. Susceptibility determinations of praseodymium and cerium in the quadrivalent state were described in 1925,[15] and later investigators[16] have examined compounds of bivalent samarium, tervalent gadolinium, and both bi- and ter-valent europium and ytterbium. The results from the various researches bear out the law that the susceptibility of a quadrivalent rare-earth metal ion approaches that of the ion of a metal with atomic number one less, but having a valency of three. Also the susceptibility of a bivalent rare-earth metal ion approaches that of the ion of a metal with atomic

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[12] *J. Amer. Chem. Soc.*, 1932, **54**, 496.

[13] *Ber.*, 1934, **67**, 1679.

[14] *Chem. Reviews*, 1935, **16**, 121.

[15] S. Meyer, *Physikal. Z.*, 1925, **26**, 51, 479.

[16] W. Klemm and J. Rockstroh, *Z. anorg. Chem.*, 1928, **176**, 181; W. Klemm and W. Schüth, *ibid.*, 1929, **184**, 352; P. W. Selwood, *J. Amer. Chem. Soc.*, 1933, **55**, 4869; 1934, **56**, 2392; G. Hughes and D. W. Pearce, *ibid.*, 1933, **55**, 3277.

number greater by one, but with a valency of three. These facts must mean that, on reduction, the third electron—the one not in use for valency purposes—is suppressed and becomes associated with the 4_4 orbital groups. On oxidation this inner group then gives up the electron as a valency unit. For example, the difference between ytterbium (at. no. 70) in the bivalent and in the tervalent state is expressed by the electronic distribution :

	K.	*L.*	*M.*	*N.*	*O.*
Yb^{3+}	2	8	18	18 + 13	8
Yb^{2+}	2	8	18	18 + 14	8

In view of the fact that the rare-earth metals differ, as far as the orbital electrons are concerned, only in the distribution in the fourth quantum group, it might be expected that the colour of their salts would be due mainly to the degree of incompleteness of this shell. Thereby colour relations might be thought to be periodic, but this idea is not substantiated by the facts, as the following table shows.

Colours of tervalent ions.

57 La	71 Lu	Colourless
58 Ce	70 Yb	,,
59 Pr	69 Tm	Green
60 Nd	68 Er	Red
62 Sa	66 Dy	Yellow
63 Eu	65 Tb	Faint rose
64 Gd		Colourless

This interesting colour sequence has been discussed by various writers, *e.g.*, L. F. Yntema [17] and J. D. Main Smith,[18] but it cannot yet be considered as fully explained. There is, incidentally, an interesting resemblance in colour in the cases of certain bi- and ter-valent ions :

At. No.	62	63	69	70
Ion	Sm^{3+}	Eu^{2+}	Tm^{3+}	Yb^{2+}
Colour	Pale yellow	Colourless	Green	Green

It should be mentioned that magnetic susceptibilities, when carefully measured, afford a most accurate means of analysis, because the magnetic susceptibilities of mixtures of rare-earth compounds are additive.

The strengths of the rare earths as bases have very frequently been determined, and the results show that there are considerable differences in this property among the various members of the group. B. S. Hopkins [19] has produced a table which gives the

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[17] *J. Amer. Chem. Soc.*, 1926, **48**, 1598.

[18] *Nature*, 1927, **120**, 583.

[19] *J. Chem. Educ.*, 1936, **13**, 363.

relative strength of any rare earth, where the strength of $Y(OH)_3$ is taken as unity.

At. No.	39	57	59	60	62	64	66
Element	Y	La	Pr	Nd	Sm	Gd	Dy
Rel. basicity	1	1300	80	47	8	3·4	0·5

It is safe to say that lanthanum hydroxide is the strongest tervalent base known. It is also important to notice that lanthanum is eleven times as basic as praseodymium, while neodymium is nearly six times as basic as samarium. The order of decreasing basicity becomes a matter of importance, because some of the most useful methods of separation are based upon the differences in this property. The latest investigations of G. Endres [20] and of B. S. Hopkins [21] and his collaborators lead with great certainty to the results that the order of decreasing basicity throughout the rare-earth group is exactly the order of increasing atomic number. If yttrium (at. no. 39) were included in the rare-earth group it would form an exception, for Hopkins [19] states that in basicity it falls between illinium (at. no. 61) and samarium (at. no. 62), and G. Endres [20] places it between gadolinium (64) and dysprosium (66).

J. Newton Friend [22] has carried out a series of solubility investigations on the selenates, nitrates, and double magnesium nitrates of lanthanum, praseodymium, and neodymium, largely with the object of facilitating the separation of these rare-earth metals.

Finally, mention should be made of the interesting results obtained by G. Jantsch and his collaborators,[23, 24] who have prepared the almost complete series of the chlorides, bromides, and iodides, and determined their melting points. It will be seen from the figure given by Jantsch [24] that the melting points are arranged very regularly, and it is noteworthy that in the first half of the series the chlorides possess the highest melting points, and in the second half the iodides. W. Klemm [25] suggests that this is due to the fact that in the second half of the group another lattice type occurs.

From this short summary of modern work on the rare earths it will be clear that the study of this group is far from exhausted. Much still remains to be done on the chemistry of anomalous valencies in spite of the work of investigators in different parts of the world,

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[20] *Z. anorg. Chem.*, 1932, **205**, 321.

[21] *J. Amer. Chem. Soc.*, 1933, **55**, 3117, 3121.

[22] *J.*, 1928, 1820; 1930, 1633, 1903; 1931, 1802; 1932, 707, 1083; 1935, 356, 824, 1430.

[23] *Z. anorg. Chem.*, 1929, **185**, 49; 1931, **201**, 207.

[24] *Ibid.*, 1932, **207**, 357.

[25] *Angew. Chem.*, 1934, **47**, 21.

and the group of elements as a whole presents many fresh problems to the courageous and resourceful investigator.

S. R. C.
W. W.

6. Some Elements and Compounds.

There has been a considerable output of interesting and important work, although in the main the year's work has followed closely along established lines. Again, full use has been made of the facilities provided by modern chemical equipment and methods.

P. W. Schenk and H. Platz [1] have announced the preparation of a hitherto unknown peroxide of phosphorus. On passing a mixture of the vapour of phosphoric oxide (P_2O_5) and oxygen at a pressure of *ca.* 1 mm. of mercury through a hot discharge tube, a bluish-violet product separated behind the discharge zone and was stable for a day at room temperature, if moisture was excluded. Its aqueous solution was colourless, and slowly liberated iodine from potassium iodide. The product is considered to contain about 2% of a new peroxide of phosphorus of the empirical formula PO_3.

The hydrides of phosphorus have recently been subjected to renewed investigation and some important facts have been disclosed. To the liquid hydrogen phosphide which accompanies gaseous phosphine when phosphorus is acted on by aqueous potassium hydroxide, the formula P_2H_4 (*M.W.* 66) has been generally ascribed, although the molecular weights of 74·4—77·0, found by L. Gattermann and W. Hausknecht,[2] are by no means in good agreement with it. The discrepancy has usually been attributed to the presence of higher homologues. Liquid hydrogen phosphide has now been carefully prepared by P. Royen and K. Hill [3] in a pure state, and density determinations are in satisfactory agreement with the formula P_2H_4. Moreover, a careful search for other homologues has demonstrated their absence. A solid yellow hydride of phosphorus is also produced during the action of aqueous potassium hydroxide on phosphorus. The empirical formula, P_2H, has long been ascribed to this substance, as the result of the work of P. Thénard,[4] and of Gattermann and Hausknecht,[2] who regarded its formation as due to a breaking up of the P_2H_4 molecule :

$$5P_2H_4 = 6PH_3 + 2P_2H$$

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[1] *Naturwiss.*, 1936, **24**, 651.

[2] *Ber.*, 1890, **23**, 1179.

[3] *Z. anorg. Chem.*, 1936, **229**, 97.

[4] *Ann. Chim. Phys.*, 1845, [iii], **14**, 5; *Annalen*, 1845, **55**, 27.

A cryoscopic determination of molecular weight by R. Schenck and E. Buch [5] raised the formula P_2H to $P_{12}H_6$. Direct estimations of phosphorus and hydrogen in the solid hydride, made by R. Schenck [6] and by A. Stock,[7] indicated a composition varying between $P_{12}H_{5\cdot45}$ and $P_{12}H_{6\cdot4}$, the difference being due, presumably, to experimental errors. P. Royen and K. Hill,[3] however, have now reinvestigated this substance and consider that the yellow hydride is not a definite compound, but that it arises from adsorption of PH_3 on amorphous yellow phosphorus, these products having been formed by the decomposition of liquid hydrogen phosphide:

$$3P_2H_4 = 2P + 4PH_3$$

It is pointed out that the analytical methods employed for the determinations of phosphorus and hydrogen are very exact (accuracy for hydrogen, $\pm 0\cdot03\%$) and the variations found are due simply to the different amounts of phosphine adsorbed according to the experimental conditions.

Royen and Hill [8] consider that they have substantiated their sorption theory by the artificial production of a similar substance by bringing phosphine into contact with amorphous phosphorus, although a product of composition higher than $P_{12}H_{4\cdot12}$ was not obtained.

Very little is known about the modifications of phosphoric oxide, or phosphorus pentoxide, as it is frequently called. Reference to any standard text-book reveals the conflicting nature of the available data. It seems agreed, however, that there is a form without a recognisable crystalline structure, and a vitreous form. Other forms, of more or less doubtful existence, are a crystalline form (*a*), produced by distillation at comparatively low temperatures, say 350°, and a second crystalline form (*b*), stated to be produced from the vitreous modification by prolonged heating and having a melting point of 569°. A third crystalline form (*c*), stable above 570°, is thought to exist in the absence of the lower-melting form. A. N. Campbell and A. J. R. Campbell [9] have investigated the amorphous, the vitreous, and the low-temperature crystalline form (*a*), produced from the amorphous form at any temperature between 350° and 600°, provided the heating be not prolonged. These workers have determined densities, solution tensions, and solubility in chloroform, and conclude that, of the three modifications, the only homogeneous form is the vitreous. This is the most stable, since it has the lowest

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[5] *Ber.*, 1904, **37**, 915.
[6] *Ibid.*, 1903, **36**, 991, 4202.
[7] *Ibid.*, 1909, **42**, 2849.
[8] *Z. anorg. Chem.*, 1936, **229**, 369.
[9] *Trans. Faraday Soc.*, 1935, **31**, 1567.

solubility and the highest density. It is suggested that, as the vitreous form is produced from the amorphous modification, a true solution of amorphous in vitreous is formed as an intermediate product. It is also pointed out that, if the two allotropes are sufficiently stable to form a true solution, their structural units must be very different.

The nitrides of the non-metals are very diverse in character and include a group distinguished by the most extraordinary stability. Prominent in this group are the nitrides of phosphorus, and although in the past much research has been done on these and allied substances, they still continue to excite the marked interest of many investigators. Published work dealing with the nitrides of phosphorus has appeared in recent years from H. Moureu[10] and his collaborators, P. Renard,[11] V. F. Postnikov and L. L. Kuzmin.[12] Phosphorus pentanitride, P_3N_5, can be obtained in good yield by A. Stock's method[13] from ammonia gas and P_2S_5, but H. Moureu and P. Rocquet[14] have described another method which uses the chloronitride of phosphorus, discovered by Liebig and prepared from phosphorus pentachloride and ammonium chloride. The simple reaction may be expressed thus :

$$Cl_2PCl_3 + H_3N = (Cl_2PN) + 3HCl$$

but the chloronitride is really the polymer $(PNCl_2)_3$. By the action of liquid ammonia, the chloronitride is changed into phospham, probably by the reaction

$$PNCl_2 + 2NH_3 = PN(NH_2)_2 + 2HCl$$

When phospham is heated in a vacuum at 380° it yields PN_2H by the reaction $PN(NH_2)_2 = PN_2H + NH_3$, and if the temperature now rises above 400°, pure P_3N_5 is obtained from the decomposition $3PN_2H = P_3N_5 + NH_3$. The pentanitride is a light amorphous powder, insoluble in cold water and the usual solvents. It is attacked only very slowly by concentrated sulphuric acid, but it is quantitatively converted into orthophosphoric acid and ammonia by sulphuric acid at the boiling point :

$$2P_3N_5 + 5H_2SO_4 + 24H_2O = 6H_3PO_4 + 5(NH_4)_2SO_4$$

It is therefore conveniently analysed by the Kjeldahl method.[12] When heated to 730° in a vacuum, P_3N_5 yields PN, which sublimes.

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[10] H. Moureu and A. M. de Ficquelmont, *Compt. rend.*, 1934, **198**, 1417; also refs. (14), (15), and (16).

[11] *Ibid.*, p. 1159; *Bull. Soc. chim.*, 1933, [iv], **53**, 692; *Ann. Chim.*, 1935, xi], **3**, 443.

[12] *J. Appl. Chem. Russia*, 1935, **8**, 429.

[13] A. Stock and B. Hoffmann, *Ber.*, 1903, **36**, 314.

[14] *Compt. rend.*, 1934, **198**, 1691.

This, according to H. Moureu and P. Rocquet,[15] can exist in two forms. The more stable red form reduces warm concentrated sulphuric acid, but this reaction is very slow in the cold. The other form obtained from P_3N_5 at temperatures in the neighbourhood of 720° is yellow, and is readily soluble in sulphuric acid, reducing it even at room temperature. Neither form shows crystal structure when examined by *X*-rays. H. Moureu and G. Wetroff [16] have added a new nitride to the list. When the products of the reaction of phosphorus trichloride on liquid ammonia are heated in a vacuum at 550°, a white, insoluble, non-volatile substance is obtained, spontaneously inflammable in air. This nitride, P_4N_6, heated above 750° in a vacuum, gives PN, which condenses in a pure state.

Until recently, the heats of formation of the metallic nitrides have been derived indirectly. Now B. Neumann, C. Kroger, and their collaborators [17] have evolved a method whereby these measurements can be made from the direct union of the metal and the gas, and their work has disclosed some very interesting facts about this chemical reaction. Certain of the metals studied would unite with nitrogen under a pressure of 5—25 atmospheres and a temperature of 500—1000° with sufficient velocity to give a measurable rise of temperature within one or two minutes. Manganese, chromium, and lithium would do this, but aluminium, beryllium, and magnesium required a catalyst, of which sodium fluoride proved to be the best. The reactions of a number of metals such as nickel, cobalt, aluminium, and beryllium were catalysed by lithium nitride. It was found that thorium must be very pure to react with nitrogen and, curiously, its reactivity was not improved by sodium fluoride. In all cases the nitrogen must be oxygen-free. A relationship has been established between the heats of formation of the nitrides and the atomic numbers of the metallic elements, and on the basis of this the authors have deduced values for the nitrides of other elements such as scandium, vanadium, and tungsten. As the ease with which a metal takes up nitrogen varies very much with its condition, this has been studied for molybdenum–iron alloys and for molybdenum by A. Sieverts and his collaborators.[18]

In 1909, A. Hantzsch [19] determined the molecular weight of chamber crystals ($HO{\cdot}SO_2{\cdot}ONO$) cryoscopically in sulphuric acid and obtained values varying from 70·8 to 72·5, compared with the

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[15] *Bull. Soc. chim.*, 1936, [v], **3**, 1801.

[16] *Compt. rend.*, 1935, **201**, 1381.

[17] *Z. anorg. Chem.*, 1931, **196**, 65; 1932, **204**, 81; **207**, 133, 145; 1934, **218**, 379.

[18] A. Sieverts and K. Brüning, *Arch. Eisenhüttenw.*, 1933—34, **7**, 641; A. Sieverts and G. Zapf, *Z. anorg. Chem.*, 1936, **229**, 161.

[19] *Z. physikal. Chem.*, 1909, **65**, 57.

calculated value of 127 for $HNSO_5$. He concluded, therefore, that this substance behaves as an electrolyte, and suggested that dissociation into NO^+ and HSO_4^- ions took place. Twenty-one years later, from an examination of the conductivity of nitrosyl perchlorate in nitromethane, Hantzsch and K. Berger [20] deduced that nitrosyl perchlorate, like nitrosyl sulphate, exists as a salt-like compound $[NO]^+[X]^-$, where $X = ClO_4$ or SO_4. A recent investigation by W. R. Angus and A. H. Leckie of the Raman spectrum of nitrosyl sulphate (chamber crystals),[21] and nitrosyl perchlorate [22] has given results which can be interpreted only on the assumption that these substances have an ionic structure.

In order to substantiate the deductions from Raman measurements, electrolytic experiments [23] were undertaken. A qualitative demonstration that nitrosyl sulphate has an ionic structure was made by electrolysing a solution of nitrosyl sulphate in sulphuric acid between a platinum anode and an iron cathode. The lower portion of a glass U-tube was filled with a concentrated solution of nitrosyl sulphate in sulphuric acid, and the upper portion of each limb filled up with more sulphuric acid; the electrodes were dipping into the acid. The iron cathode provided a source of ferrous sulphate in the cathode limb where NO^+ would be discharged. After the current had passed for some time, an intense brown colour developed in the cathode limb, which suggests that NO^+ ions are discharged at the cathode to give the well-known brown $FeSO_4,NO$. The authors conclude that, although, unfortunately, quantitative conductivity measurements have not yielded results of high accuracy, they have indicated that nitrosyl sulphate and nitrosyl perchlorate are electrolytes. No salts of nitrosylsulphuric acid could be isolated in spite of several attempts. This fact supports the view that the substance is a salt, and actually the salt-like configuration is the ionised form of the structure hitherto accepted by most chemists, $SO_2(OH)\cdot ONO$. The authors also discuss the theoretical possibility of the existence of such a radical as NO^+. The most important criterion is the ease with which a neutral molecule can lose an electron and become positively charged. To bring this about, a certain ionisation potential is required, and it follows that the lower the ionisation potential the greater the probability of the existence of that particular ion. For nitric oxide the ionisation potential is 9·5 volts.[24] The ionisation potential of $N_2 \longrightarrow N_2^+$ is very considerably higher, and that

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[20] *Z. anorg. Chem.*, 1930, **190**, 321.

[21] *Proc. Roy. Soc.*, 1935, *A*, **149**, 327.

[22] *Ibid.*, 1935, *A*, **150**, 615.

[23] W. R. Angus and A. H. Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958.

[24] J. T. Tate and P. T. Smith, *Physical Rev.*, 1932, **39**, 270.

for $O_2 \longrightarrow O_2^+$ also very much higher than that for $NO \longrightarrow NO^+$. The value for the ionisation potential of O_2 is given by R. S. Mulliken and D. S. Stevens[25] as 12·2 volts. It is clear that for the nitric oxide molecule the ionisation potential is decidedly low, as in general for diatomic molecules the value is above 10 volts. This may arise from the fact that nitric oxide is an odd-electron molecule, having 15 extranuclear electrons. When it becomes ionised it is isoelectronic with carbon monoxide and nitrogen. Since isoelectronic structures exhibit many similar properties, it is possible that the NO^+ radical is a relatively stable one.

Although nitrosoamine, $NH_2{\cdot}NO$, is probably not stable at room temperature, there is good evidence to show that R. Schwarz and H. Giese[26] have obtained this compound by the interaction of solid anhydrous ammonia and solid dinitrogen trioxide, N_2O_3, at low temperatures. The reaction was conducted at the melting point of anhydrous ammonia, and the experiments exhibit some novel features. Liquid anhydrous ammonia (*ca.* 60 c.c.) was poured into a quantity of liquid air contained in a large porcelain dish, which was covered with a loosely fitting wooden lid. The ammonia soon solidified, and after the workers' hands had been suitably protected with gloves, the ammonia and liquid air were ground with a pestle into a thin paste. Dinitrogen trioxide in a smaller amount (1—2 g.) was similarly crushed in liquid air, and the two reagents were transferred to a wide-necked flask which was rapidly connected, through a ground joint, to a pump, and the excess of liquid air removed. The reaction mixture was shaken and allowed to warm somewhat, whereupon the light blue colour of the mass changed into the orange-red colour characteristic of the nitrosoamine. After the whole of the ammonia had melted, a clear red solution remained. (Some nitrogen was evolved, and this was swept out by ammonia gas and collected in an azotometer containing dilute acid.) The ammonia was carefully distilled off, and the solution gradually assumed a deep purple-red colour. This is probably the real colour of the nitrosoamine, and the orange-red appearing in its preparation with dinitrogen trioxide may be due to admixture with nitric oxide, which has a yellow colour when dissolved in liquid ammonia. The authors represent the formation and decomposition of nitrosoamine thus :

$$N_2O_3 + 2NH_3 = (NH_4)NO_2 + H_2N{\cdot}NO$$
$$2H_2N{\cdot}NO = (NH_4)NO_2 + N_2$$

Nitrosoamine cannot be obtained in any solvent other than liquid anhydrous ammonia, for it at once breaks up into ammonium nitrite

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[25] *Physical Rev.*, 1934, **44**, 720.

[26] *Ber.*, 1934, **67**, 1108.

and nitrogen. The nitrosoamine was also formed when the dinitrogen trioxide was replaced by nitrosylsulphuric acid, $[NO]HSO_4$, nitrosyl perchlorate, $[NO]ClO_4$, or nitrosyl chloride, NOCl. The proposed formulation of the nitrosoamine is further supported by the fact that methylaniline and dinitrogen trioxide at $-5°$ yield *N*-nitrosomethylaniline, NPhMe·NO; also that nitric oxide under pressure acts on potassium amide in solid ammonia to give the nitrosoamine :

$$KNH_2 + 2NO = KNO + NH_2{\cdot}NO$$

The authors suggest two possible structures for the nitrosoamine, $H_2N{-}N{=}O$ and $H{-}N{=}N{-}OH$, of which the latter is in accordance with its deep colour, whilst the former is more consistent with its mode of formation. Probably the two forms are in tautomeric relation to one another.

In their study of the decomposition products of carbon suboxide (C_3O_2), A. Klemenc, R. Wechsberg, and G. Wagner [27] have made the fascinating observation that carbon may probably exist in a gaseous form, as dicarbon C_2. The reaction is considered to be $C_3O_2 \rightleftharpoons CO_2 + C_2$ and these authors state that at 200° the equilibrium constant $K = P_{CO} \, . P_{C_2}/P_{C_3O_2}$ is *ca.* 10^{-7}. The equilibrium is constantly disturbed by the polymerisation process, $C_2(\text{gas}) \rightarrow \text{graphite}$. Dicarbon is a carmine-red gas, soluble in water. It rapidly polymerises to a purplish-red, finely divided carbon, which gives an *X*-ray diagram identical with that of graphite. In the early stages of the decomposition of the suboxide C_3O_2, the head of the Swan band at 4737 A. is clearly visible, and this is known to be characteristic of C_2. The formation of dicarbon may be an intermediate stage in the oxidation of carbon. H. G. Grimm [28] has calculated that the change from dicarbon gas to solid carbon, as diamond, is strongly exothermic, and is 100,000 cals. The absorption spectrum of gaseous carbon suboxide has been recently studied in detail by H. W. Thompson and N. Healey.[29]

In a paper on the chemical nature of graphite, A. E. Balfour, H. L. Riley, and R. M. Robinson [30] bring forward several considerations which, in their opinion, show the aromatic character of the carbon hexagon planes in pure graphite. N. K. Adam [31] pointed out some time ago that, if one of the carbon atoms in a hexagon plane of the graphite lattice is selected, then the three valency bonds lead to

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[27] *Z. Elektrochem.*, 1934, **40**, 488; *Z. physikal. Chem.*, 1934, **170**, *A*, 97.

[28] *Z. Elektrochem.*, 1934, **40**, 461.

[29] *Proc. Roy. Soc.*, 1936, *A*, **157**, 331.

[30] *J.*, 1936, 456.

[31] *Trans. Faraday Soc.*, 1934, **30**, 57.

three aromatic hexagons, suggesting a similarity, "though this may be only superficial," between the structure of graphite and triphenylmethyl. Riley and his co-workers believe that this formal similarity is reflected in a very fundamental way in the chemical properties of these two substances. A. Frenzel and U. Hofmann[32] prepared graphite bisulphate in which the carbon hexagon planes remained intact, the hydrogen sulphate ions having penetrated between them, increasing their distance apart. Graphite monofluoride (see p. 149) is a similar type of compound, though much more stable. In these compounds, Riley states, the hexagon planes are playing the part of macro-positive radicals. The analogy between graphite and triphenylmethyl is emphasised from the fact that in liquid sulphur dioxide triphenylmethyl chloride is an electrolyte, and contains the ions Ph_3C^+ and Cl^-. On the other hand, K. Fredenhagen and G. Cadenbach[33] and K. Fredenhagen and H. Suck[34] have prepared the compounds C_8K and $C_{16}K$, and A. Schleede and M. Wellmann[35] have shown that in these compounds the alkali-metal atoms have penetrated, and formed layers between, the hexagon carbon planes. These compounds, according to Riley, are obviously analogous to the alkali-metal triphenylmethyls, and the hexagon planes are acting as macro-negative radicals. Other arguments are brought forward to support this interesting idea.

In the literature many methods are given for the preparation of cuprous oxide, but the colour of the product varies widely: it may be yellow, orange-yellow, orange, red, and even dark reddish-brown. There are marked differences of opinion as to whether the preparations with yellow and red colours should be considered as identical. In many older and also in some newer text-books, the red product is regarded as the oxide Cu_2O and the yellow and orange compounds as cuprous hydroxide. F. Gebhardt, R. Köhler, and E. Körner[36] have shown that the yellow compound obtained by reduction of Fehling's solution with glucose, gelatin, or sugar, at boiling heat, is identical with the red crystalline oxide. In order to settle the question, M. Straumanis and A. Cirulis[37] have prepared cuprous oxide by a wide range of methods and at various temperatures, and submitted the products to an X-ray investigation. The red product was obtained in a high state of purity by reduction of a solution of cupric hydroxide in concentrated ammonia with hydrazine

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[32] *Z. Elektrochem.*, 1934, **40**, 511.
[33] *Z. anorg. Chem.*, 1927, **158**, 249.
[34] *Ibid.*, 1929, **178**, 353.
[35] *Z. physikal. Chem.*, 1932, *B*, **18**, 1.
[36] *Kolloid-Z.*, 1933, **63**, 257.
[37] *Z. anorg. Chem.*, 1935, **224**, 107.

hydrate in a hydrogen atmosphere. The yellow product was isolated from the reaction between cupric nitrate in ammoniacal solution and hydrazine and 2*N*-potassium hydroxide in a nitrogen atmosphere. The yellow product was also obtained by other methods. The identity of the red and the yellow oxide was established from the fact that they had identical lattice dimensions. The yellow passes into the red modification on growth of crystallites, *e.g.*, on ignition, as is shown by the increase in sharpness and number of diffracted Röntgen lines with the redness of the material.

Lead monoxide, as is well known, occurs naturally in two crystalline forms, yellow and red. These can also be prepared in the laboratory by artificial means. The difference between the forms has been attributed to polymorphism, the red being regarded as the more stable form at the ordinary temperature and at all temperatures up to the transition point. Some years ago the existence of these two forms was in dispute, but M. P. Applebey and R. D. Reid[38] isolated the varieties in well-crystallised forms and brought forward evidence derived from solubility measurements and examination of crystalline structure which showed clearly that the two modifications were polymorphic forms. E. Rencher and M. Bassière[39] now report the results of an *X*-ray investigation of two forms of the monoxide α- and β-PbO. The α-form was obtained as an orange-yellow compound by the dehydration of lead hydroxide (produced from a lead salt and alkali) at 130°, and also by heating lead carbonate to 260°. An investigation of this modification in a dilatometer gave a sharp contraction at 530°, indicating a transition into a new form, a lemon-yellow power, which they designate β. These two forms gave distinctive *X*-ray diagrams. When the β-form was melted and allowed to solidify, the *X*-ray diagram showed that it was still β, so presumably a $\beta \longrightarrow \alpha$ transition did not occur. The thermal decomposition of lead dioxide or red lead always led to α-lead oxide, provided that the temperature was below 530°. If a sodium hydroxide solution of concentration above 30% acted on lead hydroxide at 20° a greenish-yellow β-lead oxide was formed. After long standing, this β-form slowly changed into a carmine-red α-form.

S. S. Bhatnagar and G. S. Bal[40] consider that pure nickel oxide, NiO, is green, and that black samples owe their colour to adsorbed oxygen. They also state that their magnetic-susceptibility determinations, made at 25—366°, show that the high values of χ for NiO recorded in the literature are due to traces of nickel formed by reduction during its preparation. On the other hand, W. Klemm

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[38] *J.*, 1922, **121**, 2129.

[39] *Compt. rend.*, 1936, **202**, 765.

[40] *J. Indian Chem. Soc.*, 1934, **11**, 603.

and K. Haas[41] express the view that the variable values for the magnetic susceptibility of nickel oxide, NiO, are due to partial splitting up into nickel and a higher oxide at temperatures above 400°. In an earlier Report, attention was directed to some work by (Miss) W. R. A. Hollens and J. F. Spencer[42] on the supposed sub-halide of cadmium, Cd_4Cl_7, and the so-called cadmous hydroxide and oxide, Cd_2O. The cadmium atom (at. no. 48) has the electronic structure 2, 2.6, 2.6.10, 2.6.10.0, 2, from which it is seen that the atom has two *s*-electrons in the O_1 shell and the bivalent cadmium ion a complete N_{111} shell. Both cadmium and the Cd^{++} ion must be diamagnetic, but the Cd^{+} ion with one odd electron will be paramagnetic. Thus if solutions of cadmium in molten cadmium chloride contain cadmous chloride, CdCl, in appreciable amount the system will be paramagnetic. Measurements of the solid systems, made by Hollens and Spencer, show these to be diamagnetic; hence the existence of a sub-chloride, CdCl, has to be excluded. This result has been confirmed by J. Farquharson and E. Heymann.[43] These authors point out, however, that the measurements do not exclude the existence of a bimolecular sub-chloride, Cd_2Cl_2, because such a substance would be diamagnetic. A definite verdict on this matter is given by the work of R. E. Hedges and H. Terrey,[44] who have examined by *X*-ray methods the so-called sub-halide, Cd_4Cl_7, prepared by solution of cadmium in molten cadmium chloride, and find that the structure is identical with that given by the normal chloride, $CdCl_2$, and the metal. Powder photographs of the so-called cadmous oxide, Cd_2O, prepared from Cd_4Cl_7 by decomposition with water, were taken, and compared with those from the normal oxide. It was then quite evident that the so-called sub-oxide is merely a mixture of the normal oxide with very finely divided metal. These findings are in harmony with the results obtained from other physical measurements on the solid product, *e.g.*, density, heats of solution, etc., and it must be concluded that the sub-halides and sub-oxides of cadmium are incapable of existence as solid phases.

It has always been questionable whether the formula for the higher oxides of the alkali metals M_2O_4 is not better halved. F. Ephraim[45] expresses the opinion that there is little to be said against the formulation MO_2. Nevertheless, the double formula is possibly easier to construct from the usual valency considerations. L. Pauling has recently raised the question whether the potassium

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[41] *Z. anorg. Chem.*, 1934, **219**, 82.

[42] *J.*, 1934, 1062.

[43] *Trans. Faraday Soc.*, 1935, **31**, 1004.

[44] *Ibid.*, 1936, **32**, 1614.

[45] "Inorganic Chemistry," Gurney and Jackson, London, 1926, p. 341.

oxide should not be KO_2 instead of K_2O_4. E. W. Neumann,[46] at the suggestion of L. Pauling, studied the magnetism of this peroxide, found the paramagnetism of the expected magnitude for the simpler molecule, and concluded therefore that KO_2 was really present. W. Klemm [47] has discussed the exact measurements, and states that here is a case where such measurements cannot decide between the two formulæ and that we must await further investigations, especially those of the lattice structure, before a final opinion can be given. This year the structure of potassium tetroxide has been determined by *X*-ray methods, by V. Kassatochkin and V. Kotov,[48] and they state that the formula KO_2 is supported.

J. F. Spencer and (Miss) G. T. Oddie [49] have successfully prepared lithium alum, despite the fact that the probability of its existence has been denied. To prepare the alum, molecular proportions of lithium sulphate monohydrate and the octadecahydrate of aluminium sulphate were dissolved in the minimum quantity of cold water. The solution was concentrated considerably by evaporation on a sand-bath, and cooled in a freezing mixture of ice and salt with vigorous stirring, whereupon it crystallised suddenly and deposited a mass of small crystals. The mother-liquor after a further slight concentration deposited small transparent crystals on keeping in the freezing mixture. Both crops of crystals contain H_2O, 49·0 [$Li_2SO_4,Al_2(SO_4)_3,24H_2O$ requires H_2O, 48·93%]. The crystals are isotropic, a combination of cube and octahedron. M. Mousseron and P. Gravier [50] conclude from solubility, density, viscosity, and dilatometric measurements that sodium alum is stable only between 11° and 39°. The heat of formation of $Al_2(SO_4)_3,18H_2O$ and $Na_2SO_4,10H_2O$ is −3980 g.-cals., and the heat of dissolution in water −8500 g.-cals. A stable hydrate containing $4H_2O$ has also been obtained at 15° in a vacuum. In the literature it is generally stated that two alums are known containing tervalent titanium, $Rb_2SO_4,Ti_2(SO_4)_3,24H_2O$ and the cæsium analogue. J. Meyer and H. Meissner [51] have recently attempted to extend the series, but their attempts to prepare titanium–potassium, –ammonium, and –thallous alums failed. They state that pure $RbTi(SO_4)_2,12H_2O$ could not be obtained.

In a continuation of the studies of the phosphates, H. Bassett, W. L. Bedwell, and J. B. Hutchinson [52] have examined the pyro-

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[46] *J. Chem. Physics*, 1934, **2**, 31.
[47] *Angew. Chem.*, 1935, **48**, 617.
[48] *J. Chem. Physics*, 1936, **4**, 458.
[49] *Nature*, 1936, **138**, 169.
[50] *Bull. Soc. chim.*, 1932, [iv], **51**, 1382.
[51] *J. pr. Chem.*, 1935, [ii], **143**, 70.
[52] *J.*, 1936, 1412.

phosphates of some bivalent metals, and have noted that there is a marked tendency for the formation of solid solutions containing sodium, although definite double salts also occur. They make the important suggestions (*a*) that the water molecules are distributed so as to give cations with even co-ordination numbers, and (*b*) that replacement of $[M(H_2O)_4]^{\cdot\cdot}$ by $[Na_2(H_2O)_2]^{\cdot\cdot}$ or $[M(H_2O)_2]^{\cdot\cdot}$ by $2Na^{\cdot}$ occurs owing to approximate equality of molecular volumes. In support of this view it is mentioned that the $Na_4P_2O_7,10H_2O$ which separates in large transparent crystals from solutions containing magnesium, cobalt, nickel, or zinc pyrophosphate contains a small amount of these in solid solution. This is explicable on the basis of the above theory and indicates that $Na_4P_2O_7,10H_2O$ is probably $[Na(H_2O)_4]_2^{\cdot\cdot}$ $[Na_2(H_2O)_2]^{\cdot\cdot}[P_2O_7]''''$.

Although indium is present in minute amounts in a number of minerals, it is one of the rarest of metals, and its scarcity has restricted the investigation of its chemistry. In an arc-spectrographic determination of indium in minerals, F. M. Brewer and (Miss) E. Baker [53] have made the valuable observation that indium is present in unusually large amounts in the mineral cylindrite. This mineral, obtained from the Santa Cruz mine, Poopo, Bolivia, is a sulphide of lead, antimony, and tin, and has been shown to have an indium content estimated at 0·1—1%. Brewer and Baker [54] have also found that indium is present in large traces in some chalcopyrites and as a general impurity in metallic tin, and they have described its extraction and concentration from these sources.

The subject of the nomenclature and classification of inorganic compounds is one of great and ever-increasing difficulty, and for nearly twenty years chemists of many countries have been trying to devise a systematic international nomenclature. In his lecture, delivered before the Chemical Society this year, C. Smith [55] gave an account of the agreement that has been reached, and as modern chemical nomenclature is a subject of the deepest concern to all chemists, this address deserves the closest study.

Finally, attention should be directed to the recent publication by (Sir) G. T. Morgan and F. H. Burstall,[56] which gives a survey of modern developments in inorganic chemistry.

S. R. C.
W. W.

S. R. CARTER.
W. WARDLAW.
R. WHYTLAW-GRAY.

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[53] *J.*, 1936, 1286.

[54] *Ibid.*, p. 1290.

[55] *Ibid.*, p. 1067.

[56] "Inorganic Chemistry," Heffer, Cambridge, 1936.

CRYSTALLOGRAPHY

THE change from biennial to annual publication of the report on Crystallography occurs appropriately at a time when attention has been focused on the subject by Sir William Bragg's presidential address[1] to the Royal Society summarising many of the recent advances in crystal analysis. The past history of structure determination has also been brought nearly up to date this year by the appearance of the long-awaited second volume and part of the third volume of the "Strukturbericht,"[2] the first volume of which has meanwhile become a classic. The main lines of Vol. I have been followed, and the results so far available include all inorganic structures, but not alloys, organic compounds, and fibres.

As it is impossible to cover all phases of crystallography adequately in this survey, some subjects which appear to be more suitable for biennial treatment have been left over for consideration in later Reports. This applies particularly to metals, which have been discussed at length in the two preceding Reports.

1. THE TECHNIQUE OF STRUCTURE ANALYSIS.

For all kinds of crystal structure work, more powerful X-ray tubes are highly desirable, and a notable advance in the design of rotating anode tubes has now been made by V. Linnitzki and V. Gorski.[3] They have combined the anode with a molecular pump so that the rotation of the anticathode, which formerly introduced many difficulties in construction and maintenance, is now turned to positive advantage. As far as the recording of the X-ray reflections is concerned, there are three main types of instrument that can be considered. G. Kellström's[4] new value for the viscosity of air may be taken to show, *inter alia*, the reliability of the X-ray method for the measurement of e, and there is therefore the more justification for continued work on precision measurements of lattice spacings,

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[1] *Proc. Roy. Soc.*, 1936, *A*, **157**, 697.

[2] Akademische Verlagsgesellschaft m.b.H., Leipzig, 1936 : Vol. II (1928—32) by C. Hermann, O. Lohrmann, and H. Philip; Vol. III (1932—35) by C. Gottfried and F. Schossberger.

[3] *Tech. Phys. U.S.S.R.*, 1936, **3**, 220.

[4] *Physical Rev.*, 1936, [ii], **50**, 190.

particularly by powder methods.[5] M. J. Buerger's new Weissenberg goniometer [6] is likely to prove useful for the more general examination of a crystalline species, and other cameras have also been devised,[7] including some for work at high and low temperatures [8] and low pressures.[9] It does not appear to be generally recognised, however, that many of the advantages of a vacuum can be attained more simply by filling the X-ray camera with hydrogen. Finally, for the exact measurement of intensities a new automatic ionisation spectrometer has been designed by W. A. Wooster and A. J. P. Martin.[10] The use of electrometer triodes (in conjunction with an ionisation chamber) is well established; a further advance which has been proposed [11] is the replacement of the ionisation chamber or photographic plate by a Geiger–Müller counter.

The introduction of the Patterson method of synthesis was described in last year's Report and it is already taking a definite place as a first stage in the determination of many crystal structures. One example of its use is that of silver uranyl acetate.[12] D. Harker [13] has pointed out that improvements may be introduced by making full use of the symmetry of the crystal under investigation. In the general case the Patterson series is of the form

$$P(xyz) = \Sigma_h\Sigma_k\Sigma_l|F(hkl)|^2 \cos (hx + ky + lz) \quad . \quad . \quad . \quad . \quad (1)$$

the maxima in the function P representing interatomic distances. To be manageable, however, this must be reduced to a two-dimensional series

$$Q(xz) = \Sigma_h\Sigma_l|F(h0l)|^2 \cos (hx + lz) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which, since the F's of one zone only are used, the resolution of the peaks is not very good. If, however, the b axis is a two-fold axis of symmetry, two equivalent atoms have co-ordinates (xyz) and $(\bar{x}y\bar{z})$ and the vector between them has components $(2x,0,2z)$

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[5] J. W. M. du Mond and V. L. Bollmann, *ibid.*, pp. 383, 524; W. Kossel, *Ann. Physik*, 1936, [v], **26**, 533; M. Straumanis and A. Ievins, *Z. Physik*, 1936, **98**, 461; E. R. Jette and F. Foote, *J. Chem. Physics*, 1935, **3**, 605; M. U. Cohen, *Z. Krist.*, 1936, **94**, 288, 306.

[6] *Ibid.*, p. 87.

[7] M. J. Buerger, *Amer. Min.*, 1936, **21**, 11; E. Sauter, *Z. Krist.*, 1936, **93**, 93; O. Kratky and G. Krebs, *ibid.*, **95**, 253.

[8] R. L. McFarlan, *Rev. Sci. Instr.*, 1936, [ii], **7**, 82.

[9] E. Franke, *Z. physikal. Chem.*, 1936, *B*, **31**, 454.

[10] *Proc. Roy. Soc.*, 1936, *A*, **155**, 150.

[11] W. Van der Grinten and H. Brasseur, *Nature*, 1936, **137**, 657; D. P. le Galley, *Rev. Sci. Instr.*, 1935, **6**, 279; M. Pahl and A. Faessler, *Z. Physik*, 1936, **102**, 562.

[12] I. Fankuchen, *Z. Krist.*, 1936, **94**, 212.

[13] *J. Chem. Physics*, 1936, **4**, 381.

and is represented by a maximum value of P in the plane $y = 0$. Evidently, in such a case, the x and the y co-ordinates of all the atoms can be determined by measurements of P for $y = 0$ only; (1) then becomes

$$P(x0z) = \Sigma_h\Sigma_l \cos(hx + lz) \,.\, (\Sigma_k|F(hkl)|^2) \;.\;.\;.\;.\;.\quad (3)$$

a two-dimensional Fourier series which can readily be computed. This series (3) has two advantages over (2): it gives greater resolution because all the F's are used, and it shows only interatomic vectors perpendicular to the symmetry axis, so the risk of overlapping is reduced. Similar improvements can be introduced where the crystal has other elements of symmetry, and in one of these cases the method has been applied by D. Harker to determine the crystal structure of proustite and pyrargyrite.

These methods render it necessary to carry out Fourier syntheses in the very first stages of the analysis instead of once at the end; but by means of calculating devices, such as those of J. M. Robertson [14] and A. L. Patterson [15] and the sine and cosine strips now made available by C. A. Beevers and H. Lipson,[16] a two-dimensional Fourier synthesis can be carried out in little more than a day. Robertson [17] has also described simplifications of the calculations necessary in the case of non-centrosymmetrical projections and successfully used them on the structure of resorcinol. A further valuable contribution to the literature of crystallography is "Structure Factor Tables" by (Mrs.) K. Lonsdale.[18] In these, the necessary data for Fourier synthesis and for the calculation of the structure factors have been presented for each of the 230 space groups in the form in which they can most readily be applied in actual practice. The most laborious part of structure analysis (after the experimental data have been obtained) is still the calculation of structure factors, both to derive an approximate structure by "trial and error" and to determine the phases of the coefficients in a Fourier series; the labour involved can be considerably lightened by the adoption of W. L. Bragg's proposal [19] to use contoured graphs from which phase factors can be read off directly when the co-ordinates of the atoms are given. Since it is usual to investigate only special planes of the type ($hk0$), the total number of graphs

[14] *Phil. Mag.*, 1936, **21**, [vii], 176.

[15] *Ibid.*, 1936, **22**, 753.

[16] *Proc. Physical Soc.*, 1936, **48**, 772; *Nature*, 1936, **137**, 825.

[17] *Ibid.*, **138**, 683.

[18] "Simplified Structure Factor and Electron Density Formulæ for the 230 Space Groups of Mathematical Crystallography," Bell and Sons, 1936.

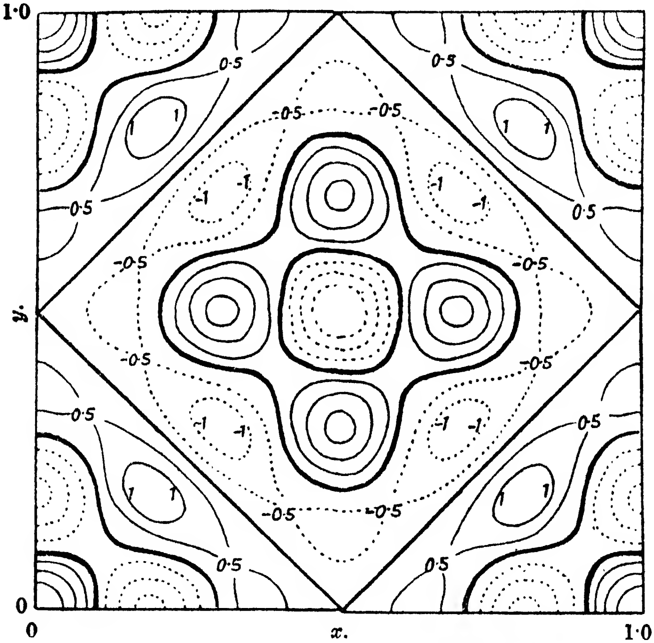
[19] *Nature*, 1936, **138**, 362; W. L. Bragg and H. Lipson, *Z. Krist.*, 1937, **95**, 383.

required is not very great, about twelve (for all values of h and k up to $h + k = 8$, say) for each of the seventeen plane groups being sufficient. Fig. 1 shows the graph for the plane (230) in any space group of the tetragonal classes $\bar{4}2m$, $4mm$, 42, and $4/mmm$. The contours give the value of the function

$$S = \cos 4\pi x \, . \cos 6\pi y + \cos 6\pi x \, . \cos 4\pi y$$

for all values of x and y between 0 and 1; the heavy lines are contours with $S = 0$, and negative contours are dotted. Thus

FIG. 1.



Contours of $S = \cos 4\pi x \, . \cos 6\pi y + \cos 6\pi x \, . \cos 4\pi y$.

the quantity S (multiplied by a power of 2 according to the space group) read off for the co-ordinates (x, y) is the contribution of an atom in the general position (xyz) *and of all the atoms in the cell related to it by the symmetry elements of the space group* to the phase factor of that particular plane. The contribution to the structure factor is then simply $2^n S f_0$. One very valuable feature of the method is that it is possible to determine by inspection of the appropriate graph how the co-ordinates of an atom or atoms must be altered to obtain a desired change in the phase factor for any plane; this shortens considerably the time necessary for trial and error analyses.

A complete set of graphs is being prepared and subjected to practical tests in various laboratories.

Several workers [20] have directed their attention to the determination of the exact form of the *f*-curves for various atoms, *viz.*, nickel, copper, zinc, cadmium, aluminium, silver, palladium, and sulphur. In the case of the hexagonal metals, cadmium and zinc, the atomic scattering factor has a low or high value according as the plane from which reflection occurs is nearly parallel or perpendicular to the basal plane. This is interpreted by G. W. Brindley [21] as being due to asymmetry of lattice vibrations—a view which, though contested by H. Hermann,[22] receives support from the work of C. Zener.[23] Zener has investigated the dependence of the Debye–Waller temperature coefficient e^{-M} upon reflection plane orientation for the case of metals of hexagonal symmetry, and finds that the ratio of M for vibrations perpendicular to and parallel to the *c*-axis is 1·80 and 1·73 for zinc and cadmium respectively. Other work on zinc,[24] while showing that the anomalous *f*-values are chiefly due to the anisotropy in the thermal vibrations, suggests that Hermann's view that the atoms themselves are anisotropic may be partly correct. Other supposed cases of anisotropic thermal vibrations are mentioned elsewhere in the Report. A critical test of atomic symmetry might be possible through the use of polarised *X*-rays as developed by W. H. George.[25]

Optical and magnetic methods have now definitely established themselves as aids to structure determination, particularly in the field of aromatic compounds, and in favourable cases it appears possible to fix the direction cosines of the plane of the molecules in the lattice to within 1°. Somewhat uncritical use has, however, sometimes been made of magnetic data, and a detailed discussion by (Mrs.) K. Lonsdale and K. S. Krishnan [26] of the precise relationships existing between molecular susceptibilities and those of the crystal as a whole is welcome. L. Pauling [27] has also discussed the

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[20] J. Laval, *Compt. rend.*, 1935, **200**, 1605; E. Nähring, *Z. Physik*, 1935, **93**, 197; C. M. Kotin and T. Losada, *Anal. Fis. Quim.*, 1935, **33**, 597; P. de la Cierva and J. Palacios, *ibid.*, p. 34; G. W. Brindley, *Phil. Mag.*, 1936, [vii], **21**, 778: G. W. Brindley and F. W. Spiers, *ibid.*, **20**, 865.

[21] *Proc. Leeds Phil. Soc.*, 1936, **3**, 200; *Phil. Mag.*, 1936, [vii], **21**, 790; *Nature*, 1936, **138**, 290.

[22] *Ibid.*, p. 290.

[23] *Physical Rev.*, 1936, [ii], **49**, 122; C. Zener and S. Bilinsky, *ibid.*, 1936, **50**, 489; see also *idem*, *ibid.*, p. 101.

[24] G. E. M. Jauncey and W. A. Bruce, *ibid.*, pp. 408, 413; R. D. Miller and E. S. Foster, *ibid.*, p. 417.

[25] *Proc. Roy. Soc.*, 1936, *A*, **156**, 96.

[26] *Ibid.*, p. 597.

[27] *J. Chem. Physics*, 1936, **4**, 673.

diamagnetism of aromatic molecules, and the relation between optical anisotropy and structure has been treated by M. Ramanadham [28] and K. S. Sundararajan.[29] Although it is unlikely, in view of the greater accessibility of other properties, that thermal conductivity will be used as an aid to structure determination, yet it is of great importance that the relationship of this property to crystal structure should be understood; a first step in this direction has been made by W. A. Wooster,[30] who has collected the available data and attempted a correlation of thermal anisotropy with structure. The possibilities and advantages of orienting molecules or particles of markedly anisotropic form by streaming or similar methods have long been realised; an interesting example is afforded by the orientation of tobacco mosaic virus " molecules " in quite dilute solutions by flow through a Lindemann glass capillary tube,[31] and a new procedure, *viz.*, sedimentation from an aqueous solution in an alternating electric field, has been applied successfully in obtaining highly oriented preparations of wool cells.[32] Such methods are capable of extension to many other imperfectly crystalline substances.

Two other applications of *X*-rays not concerned with structure analysis may be mentioned. One is the determination of particle size, which has been carried out particularly on graphite [33] from different sources and also applied to the colloid chemical behaviour of vanadium pentoxide [34] and gold sols.[35] By measurements on counted layers of fatty acid films on water, G. L. Clark and P. W. Leppla [36] have been able to obtain a direct test of the Laue equation connecting the broadening of *X*-ray lines with film thickness. The agreement is very satisfactory down to distances corresponding to only three or four fatty acid layers.

Several papers have dealt with the systematic application of morphological crystallography to the identification of chemical individuals.[37] *X*-Ray methods provide both a simpler and a more

[28] *Proc. Indian Acad. Sci.*, 1936, **3**, *A*, 43.

[29] *Z. Krist.*, 1936, **93**, 238.

[30] *Ibid.*, **95**, 138.

[31] J. D. Bernal and I. Fankuchen, *Nature*, 1936, **138**, 1051.

[32] H. J. Woods, *Proc. Leeds Phil. Soc.*, 1935—6, **3**, 132.

[33] U. Hofmann, D. Wilm, and E. Csalán, *Z. Elektrochem.*, 1936, **42**, 504; G. R. Levi and A. Baroni, *Z. Krist.*, 1936, **93**, 156; P. Corrier, *Compt. rend.*, 1936, **202**, 59; N. Ganguli, *Phil. Mag.*, 1936, [vii], **21**, 355; cf. G. I. Finch and H. Wilman, *Nature*, 1936, **137**, 271; *Proc. Roy. Soc.*, 1936, *A*, **155**, 345.

[34] J. A. A. Ketelaar, *Nature*, 1936, **137**, 317.

[35] J. B. Haley, K. Soltner, and H. Terrey, *Trans. Faraday Soc.*, 1936, **32**, 1304.

[36] *J. Amer. Chem. Soc.*, 1936, **58**, 2199.

[37] A. K. Boldirev and V. V. Dolivo-Dubrovolski, *Z. Krist.*, 1936, **93**, 321; C. Weygand, *Angew. Chem.*, 1936, **49**, 243; B. N. Delone, *Ann. Sec. Anal. Phys. Chim.*, 1936, **8**, 91; A. F. Kapustinski, *ibid.*, p. 103.

delicate means, and several attempts have been made to classify certain groups of compounds by means of powder photographs. One such "finger-print system," developed mainly for industrial purposes,[38] includes 4000 patterns from over 1000 inorganic substances, and there are several examples of its use.[39] Among organic compounds, only the method of direct, *ad hoc* comparison of two compounds suspected of being the same has been employed to any extent, as in the identification of tetrahydroartimisia ketone,[40] the barium salts of the pterins,[41] the hydrocarbon "$C_{21}H_{16}$" from cholic acid,[42] the phrenosinic acids,[43] and others.[44]

E. G. C.
D. M. C.

2. Crystal Chemistry.

Metals.—Precision measurements of the lattice constants of aluminium,[45] beryllium,[46] cadmium, osmium, and ruthenium [47] and of tantalum and vanadium [48] have been made. In addition to his usual annual survey [49] of lattice constants and other properties of the elements, M. C. Neuburger [50] has published "Die Allotropie der chemischen Elemente und die Ergebnisse der Röntgenographie." This monograph contains a critical discussion of the allotropy of all the chemical elements and is notable for a list of over 1000 references. During the past year new results have accumulated regarding the allotropy of titanium, calcium, and boron. Titanium, like zirconium, might be expected to occur in an α- and a β-form, hexagonal close-packed and cubic body-centred respectively; no convincing evidence for this had previously been obtained, however, the

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[38] J. D. Hanawalt and H. W. Rinn, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 244.

[39] A. W. Waldo, *Amer. Min.*, 1935, **20**, 575; J. N. Antipov-Karataev and B. K. Brunowski, *Kolloid-Z.*, 1936, **75**, 325.

[40] L. Ruzicka, T. Reichstein, and R. Pulver, *Helv. Chim. Acta*, 1936, **19**, 646.

[41] C. Schöpf and E. Becker, *Annalen*, 1936, **524**, 49.

[42] W. E. Bachmann, J. W. Cook, C. L. Hewitt, and J. Iball, *J.*, 1936, 54.

[43] A. C. Chibnall, S. H. Piper, and E. F. Williams, *Biochem. J.*, 1936, **30**, 100; (Miss) D. M. Crowfoot, *J.*, 1936, 716.

[44] H. J. Backer, J. Strating, and A. J. Zuithoff, *Rec. trav. chim.*, 1936, **55**, 761; M. P. Wolarowitsch, G. B. Rawitsch, and K. F. Gussjow, *Kolloid-Z.*, 1936, **76**, 338.

[45] A. Ievins and M. Straumanis, *Z. physikal. Chem.*, 1936, *B*, **33**, 265.

[46] E. A. Owen and T. L. Richards, *Phil. Mag.*, 1936, [vii], **22**, 304.

[47] E. A. Owen and E. W. Roberts, *ibid.*, p. 290.

[48] M. C. Neuburger, *Z. Krist.*, 1936, **93**, 312, 314.

[49] *Ibid.*, p. 1.

[50] Sammlung chemischer und chemische technischer Vorträge, F. Enke, Stüttgart.

irregularities in the resistance–temperature curve for the metal being attributed to impurity taken up at high temperatures. J. H. de Boer, W. G. Burgers, and J. D. Fast[51] have now shown that impurities are indeed taken up, but that the effect of these is to mask the transition which occurs (quite sharply in the absence of air) at nearly the same temperature as for zirconium (882°). *X*-Ray examination confirms that β-titanium has an A2 structure with $a = 3{\cdot}32$ A.

Calcium is known to occur in three forms, with transitions $\alpha \longrightarrow \beta$ at 300° and $\beta \longrightarrow \gamma$ at 450°, the α- and the γ-structure being cubic and hexagonal close-packed respectively. The β-form was formerly considered to be of lower symmetry, but the measurements of A. Schulze[52] indicate that it may possess an A2 lattice. The diamond-like and the graphitic form of so-called crystalline boron formerly described have probably been aluminium boride or borocarbide; S. von Naray-Szabo,[53] however, now reports an adamantine tetragonal boron with $a = 12{\cdot}55$ and $c = 10{\cdot}18$ A., and a graphitic or orthorhombic form with $a = 17{\cdot}64$, $b = 25{\cdot}0$, and $c = 10{\cdot}26$ A.

No outstanding advances have been made in the study of alloys or in the theory of metallic structures generally; a number of binary and ternary systems have been studied and further work has been done on order–disorder transformations and related topics, but the results are deferred for more comprehensive discussion in subsequent reports. An excellent and very full account of the quantum theory of metals, covering conduction, cohesion, magnetic and optical properties, and crystal structure is given by N. F. Mott and H. Jones in "The Theory of the Properties of Metals and Alloys,"[54] and W. Hume-Rothery[55] has written a most lucid review of the subject from a more descriptive point of view which should be of the utmost value to chemists and metallurgists.

Oxides.—J. A. A. Ketelaar[56] has determined the structure of vanadium pentoxide. The structure contains chains of oxygen tetrahedra linked by shared corners, accounting for the formation of elongated micelles in solution.

Structures of the spinel type have been the subject of several investigations. A. E. van Arkel, E. J. W. Verwey, and M. G. van Bruggen[57] have shown that various ferrites (MO,Fe_2O_3) are able to

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[51] *Proc. K. Akad. Wetensch. Amsterdam*, 1936, **39**, 515; W. G. Burgers and F. M. Jaeger, *Z. Krist.*, 1936, **94**, 299.

[52] *Z. Metallk.*, 1936, **28**, 55.

[53] *Naturwiss.*, 1936, **24**, 77.

[54] International Monographs on Physics, Clarendon Press, Oxford, 1936.

[55] "The Structure of Metals and Alloys," Institute of Metals, 1936.

[56] *Z. Krist.*, 1936, **95**, 28.

[57] *Rec. trav. chim.*, 1936, **55**, 331, 340.

dissolve excess Fe_2O_3 without change of (spinel) structure. This is explained by the stability of the anion framework, which is the same for γ-Fe_2O_3 as for the ferrites, the former having on the average $2\frac{2}{3}$ vacant cation positions per unit cell. In a solid solution of Fe_2O_3 in ferrite the number of vacant positions diminishes, with consequent stabilisation of the γ-Fe_2O_3 structure. These workers show that the maximum in the magnetisation curve corresponds to the maximum solubility; the dissolved Fe_2O_3 takes up the ferromagnetic γ-lattice, but when the solubility limit is transcended, the system becomes a two-phase conglomerate containing non-magnetic α-Fe_2O_3 so that the total magnetisation of the mixture is lowered. The coincidence of the solubility limit in certain cases with the composition $2MO,3Fe_2O_3$ is probably accidental, and is apparently not due, as has been suggested,[58] to the formation of a new type of ferrite.

Trimanganese tetroxide, Mn_3O_4, and ferric oxide, Fe_2O_3, form (above 800°) a continuous series of solid solutions from 100% to 14% of the former with a gradual change of structure from the tetragonal (distorted spinel) structure of Mn_3O_4 to the true spinel lattice; at lower temperatures solid solution still occurs but with the structure of Mn_2O_3 (C-modification of the sesquioxides). The solubilities in ferric oxide of oxides with the sodium chloride structure were also studied; FeO–Fe_2O_3 mixtures have only a very limited range of homogeneity, but NiO and MgO appear to form solutions over a wider range. Some ferrites have rhombohedral symmetry; [59] they may possibly possess structures of the hæmatite type. The dominating influence of the anion arrangement is illustrated by some observations of R. Mehl and E. L. McCandless [60] on the orientation of oxide films on iron. Fe_3O_4 films formed by the decomposition of ferrous oxide have identical orientation with the parent crystal; the same relation holds when ferrous oxide is obtained on the surface of the magnetite crystals by reduction.

E. J. W. Verwey and J. H. de Boer [61] suggest that, whereas Mn_3O_4 and Co_3O_4 have true spinel structures $M^{IV}M_2^{II}O_4$ (the former being distorted tetragonally on account of the lower symmetry of the Mn^{IV} ion), yet Fe_3O_4 is a solid solution FeO,Fe_2O_3 or $Fe^{III}(Fe^{II}Fe^{III})O_4$, half the tervalent cations occupying tetrahedral positions in the spinel structure, and the other half sharing the octahedral positions at random with the ferrous ions. Bond distances and X-ray

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[58] R. S. Hilpert and R. Scheveinhagen, *Z. physikal. Chem.*, 1935, *B*, **31**, 1.

[59] W. Soller and A. J. Thompson, *Physical Rev.*, 1935, [ii], **47**, 644; A. Krause, A. Ernst, S. Gawrych, and W. Kocay, *Z. anorg. Chem.*, 1936, **228**, 352.

[60] *Nature*, 1936, **137**, 702.

[61] *Rec. trav. chim.*, 1936, **55**, 531.

reflection intensities are considered to support these views, although it seems doubtful whether either can be relied upon to distinguish unequivocally between the very closely similar structures in question. With the proposed distribution of ions in magnetite, an electron passing from Fe^{++} to Fe^{+++} is in the same energy state finally as initially, and the probability of a transition is therefore reasonably high, in agreement with the high conductivity of Fe_3O_4 as compared with Co_3O_4 or Mn_3O_4. It is of interest to enquire whether these considerations can be applied quantitatively to other compounds, *e.g.*, nickelous and ferrous oxides and ferrous, cobaltous, and cuprous sulphides, in which there is normally a cation deficiency, and therefore presumably a proportion of cations in higher valency states. Although experiments [62] suggest that there is a close relation between cation deficiency and conductivity, the results for Fe_3O_4 and Co_3O_4 are very similar, and the conductivity of the latter is apparently not so greatly inferior to that of magnetite as Verwey and de Boer have supposed; moreover, the necessity of assuming quadrivalent cobalt ions is a weakness in their hypothesis. More quantitative measurements of conductivity (and also of magnetic susceptibility) in relation to composition, radius ratios, and other factors appear to be necessary before the structures of these oxides can be regarded as fully elucidated.

Oxides of tungsten [W_4O_{11}, $W_4O_{10}(OH)_2$, and $W_{12}O_{32}(OH)_2$] in which the metal appears to be present with a lower valency than six have been obtained by F. Ebert and H. Flasch [63]; it is difficult, however, to exclude the possibility of the presence of hydrogen ions in these compounds. Their cell dimensions show that they are very closely related to WO_3.

It has been suggested [64] that quartz assumes a new crystalline form below —183·5°, but other workers [65] have not confirmed this. Further work also appears to be necessary before the statements [66] that the lattice of α-quartz is deformed to the extent of 2—3% in agate and finely ground sand can be accepted. B. E. Warren and his co-workers,[67] continuing their studies of oxide glasses, have obtained much more precise results by the application of a generalised Fourier

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[62] C. Wagner, *Z. tech. Physik*, 1936, **16**, 327; C. Wagner and E. Koch, *Z. physikal. Chem.*, 1936, *B*, **32**, 439.

[63] *Z. anorg. Chem.*, 1935, **226**, 65.

[64] H. Osterberg, *Physical Rev.*, 1936, [ii], **49**, 552.

[65] H. Dobberstein, *Naturwiss.*, 1936, **24**, 414; L. Balamuth, F. Rose, and S. L. Quimby, *Physical Rev.*, 1936, [ii], **49**, 703.

[66] N. A. Schischakow, *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **1**, 19.

[67] B. E. Warren and O. Morningstar, *Physical Rev.*, 1935, [ii], **47**, 808; B. E. Warren, H. Krutter, and O. Morningstar, *J. Amer. Ceram. Soc.*, 1936, **19**, 202.

method; the existence of tetrahedral networks in silica with Si–O = 1·60 A. is definitely confirmed, and vitreous boric oxide is shown to consist of a network in which each boron is surrounded by three oxygens at 1·39 A. as in crystalline borates. In both cases the oxygen atoms are shared between only two cations, thus conferring a considerable degree of flexibility upon the network, so that the irregular glass structure has a configuration almost as stable as the crystalline arrangement. N. A. Schischakow [66] and N. Valenkof and E. Porai-Koschitz [68] have studied the transition from vitreous silica to cristobalite.

Silicates.—Further work has been done on clay minerals; the structures previously assigned to dickite and kaolinite have been confirmed by C. J. Ksanda and T. W. Barth [69] and by S. B. Hendricks [70] respectively, and the latter has also studied anauxite. J. W. Gruner [71] has shown that glauconite has a mica-type of structure with a higher Si : Al ratio; some silicon may possibly occupy 6-co-ordinated cation positions. F. A. Bannister and M. H. Hey [72] have continued their studies of zeolites with measurements on scolecite, metascolecite, and ettringite; the first is shown to be iso-structural with natrolite and its transition to metascolecite has been investigated. The cubic mineral pollucite ($Cs_2Si_4Al_2O_{12},H_2O$) appears to be related to the zeolites.[73]

E. Podschus, V. Hofmann, and K. Leschewski [74] have made a detailed study of ultramarine-blue and several related substances. The highly symmetrical structure proposed for the ultramarines by F. M. Jaeger,[75] although undoubtedly correct in essentials, was not entirely satisfactory from the point of view of interatomic distances or of *X*-ray reflection intensities. The structure now determined is analogous to that of hauyne and nosean [76] and is less symmetrical and less rigid than that suggested by Jaeger, accounting in a satisfactory manner for the variation in cell dimension when the sodium of ultramarine-blue is replaced by other alkalis. Leschewski and his co-workers consider it unnecessary to assume that the sodium ions and sulphur atoms are mobile; for the sodium, they emphasise that careful analyses never show more than eight ions per unit cell, and these can be located definitely on eight three-

[68] *Nature*, 1936, **137**, 273; cf. G. Peyronel, *Z. Krist.*, 1936, **95**, 274.

[69] *Amer. Min.*, 1935, **20**, 631.

[70] *Z. Krist.*, 1936, **95**, 247.

[71] *Amer. Min.*, 1935, **20**, 699.

[72] *Min. Mag.*, 1936, **24**, 324; *idem*, *ibid.*, p. 227.

[73] H. Strunz, *Z. Krist.*, 1936, **95**, 1.

[74] *Z. anorg. Chem.*, 1936, **228**, 305.

[75] *Trans. Faraday Soc.*, 1929, **25**, 320.

[76] F. Machatschki, *Centr. Min.*, *A*, 1934, **5**, 136.

fold positions in the lattice. The sulphur is best accounted for (in agreement with the chemical evidence) by dividing it into (*a*) sulphur ions and (*b*) S_2 molecules, distributed statistically over the twelve-fold positions; a sharp distinction between the two is not possible. There is some evidence from these compounds that the thermal vibrations of the alkali ions may have the symmetry of their environment.[77] The colour of ultramarine-blue is attributed to the S_2 groups.

Sulphides.—That close crystallo-chemical relationships exist between germanium and silicon is well known; [78] attention was drawn in last year's Report (p. 209) to the new type of fibrous structure exhibited by SiS_2, and the determination of the structure of GeS_2 by W. H. Zachariasen [79] is therefore of considerable interest. As in SiS_2, each cation is surrounded by four sulphur atoms in a slightly distorted tetrahedron, the Ge–S distance being 2·19 A. (cf. 2·26 from sum of tetrahedral radii, and 2·47 in the monosulphide), but the linking of tetrahedra is three-dimensional, giving rise to a structure which is much more like that of SiO_2 than that of SiS_2. The sulphur bond angle is 103°.

The high-temperature modifications of the cuprous and argentous sulphides, selenides, and tellurides have one of two structures,[80] according as the cation/anion radius ratio is greater or less than 0·6. In the former category are α-Ag_2S and α-Ag_2Se, in which the silver ions are distributed statistically in the interstices of a cubic body-centred arrangement of anions, whereas in the unit cells of α-Ag_2Te, α-Cu_2Se, and α-Cu_2S four anions and four metal ions form a zinc-blende structure, with the remaining cations distributed statistically. α-Cuprous telluride is not cubic, and cuprous sulphide is deficient in copper, its formula being approximately Cu_9S_5. Similarly cobaltous sulphide (nickel arsenide type) is said [81] to be stable only when slightly deficient in cobalt; in both these cases it is noteworthy that the radius ratio is very near the limiting value for the structure concerned. Two other sulphides of cobalt, Co_6S_5 and Co_9S_8, are reported; both are based on a cubic close-packing of sulphur, and have similar cell dimensions. Photographs of Co_9S_8 are almost identical with those of pentlandite,[82] suggesting the formula $(Ni,Fe)_9S_8$ for the latter, in better accord with the observed density. The transition from γ-NiS (millerite) to β-NiS (nickel

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[77] See p. 200.

[78] *E.g.*, W. Schütz, *Z. physikal. Chem.*, 1936, *B*, **31**, 292.

[79] *J. Chem. Physics*, 1936, **4**, 618.

[80] P. Rahlfs, *Z. physikal. Chem.*, 1936, *B*, **31**, 157.

[81] H. Hülsmann, F. Weibke, and K. Meisel, *Z. anorg. Chem.*, 1936, **227**, 113.

[82] M. Lindqvist, D. Lundqvist, and A. Westgren, *Svensk Kem. Tidskr.*, 1936, **48**, 156.

arsenide type) has been studied by G. R. Levi and A. Baroni,[83] and by W. Biltz *et al.*[84]; the transition temperature is 396°. W. Biltz and J. Laar [85] have confirmed the existence of Pd_4S, Pd_5S_2, and PdS_2, and a study of hauerite [86] (MnS_2) has been made. M. J. Buerger [87] has discussed the arsenopyrite structure in detail, and shows how it may be regarded as a superstructure based on the marcasite type; several new examples of this structure are recorded.

D. Harker has applied his modified Patterson's method of analysis [88] to proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3. The two structures, which are almost identical, contain continuous $(AgS)_\infty$ groups in the form of trigonal spirals, the bond angles for sulphur and silver being 83° and 165° respectively, while the length of the Ag–S bond is 2·40 A. Each arsenic (or antimony) is bonded to three sulphur atoms in a flattened pyramid. W. V. Medlin [89] has used B. E. Warren and E. Gingrich's method [90] to find the radial distribution of atoms in realgar, AsS, and orpiment, As_2S_3. The results, which are remarkably similar for the two compounds, are interesting as showing the possibilities and limitations of results based on visual estimation of intensities in powder photographs; for these two substances the first two or three peaks in the distribution curve can be related to the appropriate atomic distances without difficulty, but in other cases (*e.g.*, $CaHgBr_4$) interpretation is more difficult.

A study of berthierite, $FeSb_2S_4$, has been made.[91]

Halides.—By means of a modified Debye–Scherrer method M. Straumanis and A. Ievins [92] have determined the cell dimensions of NaCl and rock-salt with, it is claimed, greater accuracy than any yet attained. The value for rock-salt ($5{\cdot}6276_8 \pm 0{\cdot}0000_5$ A.) differs by 0·00032 A. from that obtained by Siegbahn.

Radium fluoride has the fluorite structure [93]; the radius of the radium ion (*C.N.* = 6) is 1·52 A. On the other hand, thallous fluoride [94] has a new type of (orthorhombic) structure which may be regarded as a deformed sodium chloride lattice, and the iodide [95]

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[83] *Z. Krist.*, 1936, **92,** 210.

[84] *Z. anorg. Chem.*, 1936, **228,** 275.

[85] *Ibid.*, p. 257.

[86] W. Biltz and F. Wiechmann, *ibid.*, p. 268.

[87] *Z. Krist.*, 1936, **95,** 114.

[88] See p. 197.

[89] *J. Amer. Chem. Soc.*, 1936, **58,** 1590.

[90] *Physical Rev.*, 1934, **46,** 368.

[91] M. J. Buerger, *Amer. Min.*, 1936, **21,** 442.

[92] *Z. Physik*, 1936, **102,** 353.

[93] G. E. R. Schulze, *Z. physikal. Chem.*, 1936, *B*, **32,** 430.

[94] J. A. A. Ketelaar, *Z. Krist.*, 1935, **92,** 30.

[95] L. Helmholz, *ibid.*, 1936, **95,** 129.

is also orthorhombic with a semi-layer lattice in which each ion has five near neighbours.

G. Wagner and L. Lippert[96] have studied transformations between the sodium chloride and the cæsium chloride lattice; rubidium chloride when condensed from vapour on a surface at −190° has the latter type, reverting to the normal former type at room temperature. A thermodynamic study of the transformation of ammonium bromide at −39° has been made,[97] and J. Weigle and H. Saini[98] have shown how its tetragonal structure below this temperature is obtained by slight deformation of the normal cubic structure. The energy relations of super-lattices in mixed crystals have been discussed by H. O'Daniel[99] with special reference to alkali halides; he concludes that both NaCl–AgCl and TlCl–CsCl should give rise to super-lattice structures, but the experimental results are not in agreement with the theory.

Hydrous Oxides and Salts.—Although there is a tendency in some quarters to ignore the distinction between the true hydrogen bond and the less symmetrical hydroxyl bond, the significance of these linkages is now generally appreciated, and examples of both in hydrated compounds continue to accumulate. A wave-mechanical treatment of the problem[1] shows that both symmetrical and unsymmetrical states of the system O–H–O must exist.

Manganite, Mn(OH)O, as anticipated, has a structure of the diaspore type, but the lattice now determined[2] is monoclinic, with a larger cell than that formerly proposed. As in diaspore, the close approach of oxygen atoms (2·65 A.) indicates the existence of hydroxyl bonds, which, however, link the structure together in sheets, giving rise to (010) cleavage. The octahedron of oxygens around each cation is so much distorted that the manganese has square co-ordination rather than octahedral. Unfortunately, it is difficult to judge the accuracy of the parameters in this interesting structure from the published qualitative comparison of intensities.

Sb_2O_4, Sb_6O_{13}, and Sb_2O_5 are all known to possess structures which are essentially that of senarmontite, and it is therefore not surprising to find that Sb_2O_5,H_2O has the same space group and similar cell dimensions to Sb_2O_3.[3] It is noteworthy that the higher

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[96] *Z. physikal. Chem.*, 1936, *B*, **31**, 263; **33**, 297.

[97] A. Smits, J. A. A. Ketelaar, and G. T. Müller, *ibid.*, 1936, *A*, **175**, 359.

[98] *Helv. Physica Acta*, 1936, **9**, 515.

[99] *Z. Krist.*, 1935, **92**, 221.

[1] R. H. Gillette and A. Sherman, *J. Amer. Chem. Soc.*, 1936, **58**, 1135; cf. M. L. Huggins, *J. Physical Chem.*, 1936, **40**, 723.

[2] M. J. Buerger, *Z. Krist.*, 1936, **95**, 163; cf. J. Garrido, *Bull. Soc. franç. Min.*, 1935, **58**, 224.

[3] G. Natta and M. Baccaredda, *Gazzetta*, 1936, **66**, 308.

oxides of antimony as usually prepared contain a considerable amount of water, which probably plays a part in stabilising the oxygen-rich senarmontite structures by making possible the formation of hydroxyl bonds.

The dihydrate of boron fluoride has almost identical cell dimensions with ammonium perchlorate, from which it is concluded [4] that its structure is $(OH_3)^+(BF_3OH)^-$; also, from the resemblance of the powder diagrams of nitric acid monohydrate and phosphoric acid it is inferred [5] that the former may be orthonitric acid, H_3NO_4.

Substances of the type $M(Hal)_2,3M(OH)_2$ ($M = Co$ or Ni) have simple layer lattices in which there is a statistical distribution of halogen and hydroxyl.[6] Space groups of three hydrates of sodium pyroborate, $Na_2B_4D_7$, have been determined.[7]

Complex Ions.—Linear ions. V. Kassatochkin and V. Kotov [8] report that " potassium tetroxide," KO_2, has the same structure as strontium and barium peroxides (CaC_2 type). This substance is thus definitely not K_2O_4 but contains the singly charged O_2^- ion; the O–O separation is given as 1·28 A., a value which appears slightly high by comparison with the distance 1·31 A. in the peroxides, since O_2^- is presumably a resonance structure between $O{=}O$ and $^-O{-}O^-$. A preliminary note [9] on the structure of NH_4ClBrI suggests that it is closely similar to that of ammonium di-iodide; the $BrICl^-$ ion is linear, with the iodine at its centre. L. K. Frevel [10] has made quantitative studies of several azides, and finds that the N–N distances in the potassium, sodium, and ammonium salts are 1·145, 1·150, and 1·166 A., respectively. These distances are in agreement with the accepted formulation of the linear azide ion; if it is assumed that the empirical function of L. Pauling, L. O. Brockway and J. Y. Beach [11] can be applied to variations between $N{=}N$ and $N{\equiv}N$, 1·15 A. corresponds to about 30% of triple-bond function, and 1·165 A. to about 24%. It is noteworthy that although the radius of NH_4^+ is considerably greater than that of K^+, each ammonium ion in ammonium azide is surrounded tetrahedrally by four azide nitrogens at exactly the same distance (2·96 A.) as the shortest K–N distance in the potassium salt; this relative shortening of the cation–nitrogen distance indicates the formation of hydrogen, or

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[4] L. J. Klinkenberg and J. A. A. Ketelaar, *Rec. trav. chim.*, 1935, **54**, 959.

[5] E. Zintl and W. Haucke, *Z. physikal. Chem.*, 1935, **174**, 312.

[6] W. Feitknecht, *Helv. Chim. Acta*, 1936, **19**, 467; W. Feitknecht and A. Collet, *ibid.*, p. 831.

[7] W. Minder, *Z. Krist.*, 1936, **92**, 301.

[8] *J. Chem. Physics*, 1936, **4**, 458.

[9] R. C. L. Mooney, *Physical Rev.*, 1935, [ii], **47**, 807.

[10] *J. Amer. Chem. Soc.*, 1936, **58**, 779.

[11] *Ibid.*, 1935, **57**, 2705. See this vol., p. 45.

rather "imino," bonds. Silver azide contains linear azide ions with N–N = 1·18 ± 0·04 A.[12]

AX_3 *Ions.* The cell dimensions[13] of potassium hydrogen carbonate suggest that its structure is related to that of the sodium salt, but the proposed orientation of the carbonate ions is very different, and earlier magnetic measurements[14] show that the CO_3 groups are considerably inclined to each other. Sodium carbonate monohydrate has also been studied[15] by the Patterson method; the oxygen–water separation is given as 2·69—2·72 A.

AX_4 *Ions.* The cell dimensions of the anhydrous and the monohydrated sulphates of the magnesium series have been determined from powder photographs by F. Hammel,[16] and the first case of isomorphism between tellurates and sulphates (potassium salts) has been recorded.[17] W. Schütz[18] has demonstrated the isomorphism of the ions $[GeO_4]^{4-}$ and $[GeF_6]^{2-}$ with $[SiO_4]^{4-}$ and $[SiF_6]^{2-}$ respectively.

The structure of silver phosphate, Ag_3PO_4, has been determined in greater detail by L. Helmholz,[19] who finds the P–O distance to be 1·61 A. This is greater than in dipotassium hydrogen phosphate and is attributed to the formation of covalent bonds between oxygen and silver (Ag–O = 2·34 A.). In order to obtain satisfactory agreement between observed and calculated intensities, it was necessary to assume the thermal vibrations of the silver atoms to have tetragonal symmetry, and the ratio of the amplitudes along and perpendicular to the tetragonal axis was calculated (cf. the work of Brindley and others, p. 200).

Strong forces between anion and cation are suggested also in the structure of hydrated cadmium sulphate, $3CdSO_4,8H_2O$,[19a] where the oxygen-oxygen linkages on the whole are weak.

C. Finbak and O. Hassel[20] have studied the cubic high-temperature forms of the alkali perchlorates and borofluorides. By assuming rotation of the $[ClO_4]^-$ and $[BF_4]^-$ ions, they deduce a structure for which both the interatomic distances (Cl–O = 1·55 and B–F = 1·48 A.) and the agreement between observed and the calculated intensities are more satisfactory than for the structures previously

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[12] M. Bassière, *Bull. Soc. franç. Min.*, 1935, **58**, 333; *Compt. rend.*, 1935, **201**, 735.

[13] J. Dhar, *Current Sci.*, 1936, **4**, 867.

[14] A. Mookherjee, *Physical Rev.*, 1934, [ii], **45**, 844.

[15] J. P. Harper, *Z. Krist.*, 1936, **95**, 266.

[16] *Compt. rend.*, 1936, **202**, 57, 2147.

[17] M. Patry, *ibid.*, p. 1516.

[18] *Z. physikal. Chem.*, 1936, *B*, **31**, 292.

[19] *J. Chem. Physics*, 1936, **4**, 316.

[19a] H. Lipson, *Proc. Roy. Soc.*, 1936, *A*, **156**, 462.

[20] *Z. physikal. Chem.*, 1936, *B*, **32**, 130, 433.

proposed. They conclude that rotation of the anions also occurs in the cubic hexafluorophosphates.

The hydrates of calcium sulphate have been the subject of several investigations during the past year. The structure of gypsum has been worked out in detail by W. A. Wooster;[21] it is built up of layers of sulphate and calcium ions parallel to the cleavage plane (010), linked together by layers of water molecules. Each water molecule forms two hydroxyl bonds (length 2·70 A.) with oxygen atoms of sulphate groups in successive layers and one ionic link with a calcium atom (2·44 A.). A structure proposed for calcium sulphate hemihydrate[22] is based on cell dimensions and symmetry different from those previously found,[23] and is not in agreement with the work of H. B. Weiser, W. O. Milligan, and W. C. Eckholm,[24] who found that the water is not zeolitic, and that the dehydration product has a lattice which, although closely similar to, is not identical with that of the hemihydrate. It appears still to be uncertain whether the "soluble anhydrite" first prepared by van't Hoff by the action of nitric acid on gypsum is identical with the dehydrated hemihydrate.

$[AX_6]$ *Ions.* J. Beintema,[25] from a study of the antimonates of magnesium, nickel, and barium, concludes that part of the water with which these compounds crystallise goes to form the octahedral complex $[Sb(OH)_6]^-$. A. F. Wells[26] has shown that in $Ag[Co(NH_3)_2(NO_2)_4]$, contrary to the chemical evidence, the complex ion has a *trans*-configuration. The structure is a distorted cubic close-packing of the octahedral complexes as in *trans*-$[PtCl_4(NH_3)_2]$[27] with the cations in the interstices.

As a result of the approximately spherical form of the large $[RX_6]$ ion, most structures involving it are based on cubic close-packing. Thus in many substances of the type $A_nM[RX_6]$ ($A =$ alkali metal; $n = 0, 1,$ or 2) the metals M and R occupy the positions (000) and ($\frac{1}{2}$00) of sodium and chlorine in a rock-salt lattice, the alkali ions being at the centres ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) of small cubes formed by 4M and 4R. Recent examples of this are afforded by complex nitrites (*e.g.*, $K_2Pb[Ni(NO_2)_6]$)[28] and by Prussian-blue and related sub-

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[21] *Z. Krist.*, 1936, **94**, 375.

[22] W. A. Caspari, *Proc. Roy. Soc.*, 1936, *A*, **155**, 41.

[23] P. Gallitelli and W. Büssem, *Per. Min.*, 1933, **4**, 1.

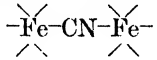
[24] *J. Amer. Chem. Soc.*, 1936, **58**, 1261; cf. P. Gaubert, *Bull. Soc. franç. Min.*, 1934, **57**, 252.

[25] *Proc. K. Akad. Wetensch. Amsterdam*, 1936, **39**, 241, 652.

[26] *Z. Krist.*, 1936, **95**, 74.

[27] E. G. Cox and G. H. Preston, *J.*, 1933, 1089.

[28] L. Cambi and A. Ferrari, *Gazzetta*, 1935, **65**, 1162; M. van Driel and H. J. Verweel, *Z. Krist.*, 1936, **137**, 577.

stances.[29] In the latter case the rock-salt structure of the $Fe[Fe(CN)_6]$ system appears to be particularly stable; ferrous alkali ferrocyanides, $A_2Fe^{II}[Fe^{II}(CN)_6]$, readily lose half their alkali, and with very little change of the remainder of the lattice are oxidised to Prussian-blue, $AFe[Fe(CN)_6]$, which again can be oxidised to Berlin-blue, $Fe^{III}[Fe^{III}(CN)_6]$, without serious alteration in the structure other than loss of alkali. Analogous compounds in which ruthenium or copper replaces part of the iron have been prepared and have similar structures. It should perhaps be pointed out that the *X*-ray evidence available does not distinguish between the formulæ $AFe^{II}[Fe^{III}(CN)_6]$ and $AFe^{III}[Fe^{II}(CN)_6]$; a further point of interest is that, in the ferrous ferrocyanide and Berlin-blue, all the iron atoms appear to be equivalent. This might be taken to indicate that individual hexacovalent ferro- or ferri-cyanide groups do not exist in the crystal as such, and that a continuous three-dimensional network  $-Fe-CN-Fe-$ extends through the lattice. This view, while attractive in many respects, is not without its difficulties (*e.g.*, the same crystallographic equivalence of atoms is observed in the mercury atoms of $K_2Hg[Hg(NO_2)_6]$), and the more detailed analysis of these interesting compounds must be awaited before any certain conclusions can be drawn.

Co-ordination complexes. In many cases the analysis of co-ordination compounds has been carried far enough to determine the configuration of a central metal atom only; in others, complete structure determinations have been made. It is probable, however, that the study of such compounds will in future be more frequently pursued to completeness, not only for stereochemical reasons, but also in order to determine the structure of organic molecules, owing to the technical advantages resulting from the presence of a symmetrically placed metal atom.

Much additional information on the distribution of the valencies of quadricovalent metal atoms has been obtained and there is increasing evidence in favour of the view that bond distribution and principal valency are closely connected, the configuration of the bonds in many cases changing from tetrahedral to planar as the state of oxidation of the atom alters. The implications of this would seem to merit attention from a theoretical point of view.

In addition to the complete structure determinations by J. M. Robertson on metal derivatives of phthalocyanins (see p. 215), several reasonably detailed analyses have been carried out. D. Harker [30] has shown that cupric chloride dihydrate, $CuCl_2,2H_2O$,

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[29] J. F. Keggin and F. D. Miles, *Nature*, 1936, **137**, 577.

[30] *Z. Krist.*, 1936, **93**, 136.

is a true quadricovalent compound in which, in agreement with earlier work, the copper valencies are coplanar. From a comparison of interatomic distances, Harker was led to suggest that the $CuCl_2,2H_2O$ complex occurs in $K_2CuCl_4,2H_2O$, which should therefore be written $K_2[CuCl_2,2H_2O]Cl_2$. An analysis[31] of $(NH_4)_2CuCl_4,2H_2O$ gives interatomic distances which confirm this. On the other hand, the water molecules in $K[AuBr_4],2H_2O$ are not co-ordinated to the metal atom.[32]

H. Brasseur and A. de Rassenfosse,[32a] continuing their investigations of complex cyanides and related compounds, have shown that barium cadmichloride tetrahydrate, $BaCdCl_4,4H_2O$, and the corresponding cadmibromide have cell dimensions very closely similar to those of barium platinocyanide tetrahydrate. Their inference that the ion $[CdCl_4]''$ has nearly the same form and dimensions as $[Pt(CN)_4]''$ must await confirmation by more detailed studies, since it is quite possible that the anions in these compounds are of the form $[MX_4(H_2O)_2]''$.

The higher hydrate of 12-phosphotungstic acid, $H_3PW_{12}O_{40},29H_2O$,[33] is of special interest. The anions $(PW_{12}O_{40})^{-3}$ (which are identical with those found by J. F. Keggin in the pentahydrate) are held together almost entirely by water molecules; anions and groups of $29H_2O$ lie on interpenetrating diamond lattices. A noteworthy feature is the constancy of both the H_2O–O and the H_2O–H_2O distance, which scarcely vary by more than the experimental error from the value 2·86 A. This is the more remarkable since a water molecule may be attached by three, four, or seven such bonds to neighbouring oxygen atoms or water molecules.

Other co-ordination compounds are discussed in the Report on Inorganic Chemistry.[34]

E. G. C.

3. Molecular Crystals.

Until this last year exact *X*-ray analyses of organic compounds have always depended on some preliminary knowledge of the structure of the molecules concerned. J. M. Robertson has now achieved in his work on the phthalocyanines[1] the first absolutely direct analysis of an organic molecule, and one which does not involve even the assumption of the presence of discrete atoms.

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[31] A. Silberstein, *Compt. rend.*, 1936, **202**, 1196.

[32] See this vol., p. 164.

[32a] *Z. Krist.*, 1936, **95**, 474; *Bull. Soc. roy. Sci. Liège*, 1936, No. 5, 125; Nos. 8–10, 199.

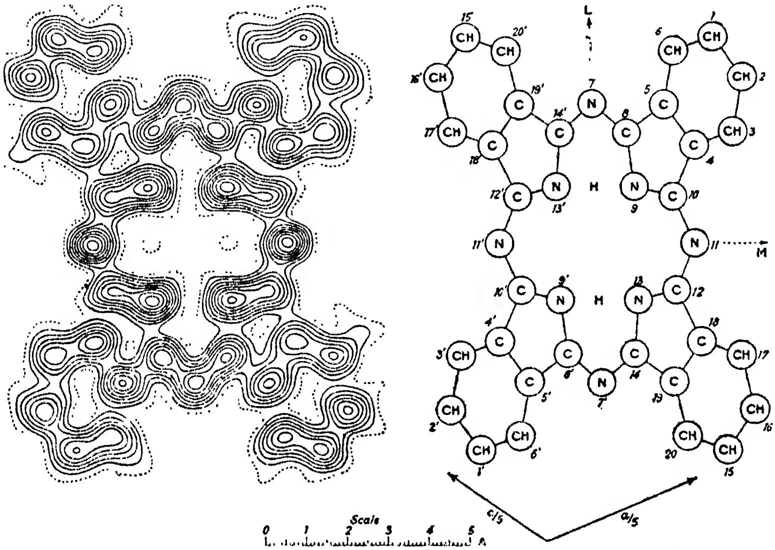
[33] A. J. Bradley and J. W. Illingworth, *Proc. Roy. Soc.*, 1936, *A*, **157**, 113.

[34] See this vol., p. 157.

[1] *J.*, 1936, 1195.

The success of this analysis depends upon the fulfilment of two conditions. In the first place the phthalocyanines crystallise in a molecular arrangement having centres of symmetry at which, by chemical means, different metal atoms can be inserted without appreciably disturbing the crystal structure. The *F* values directly calculated from the intensities of the *X*-ray reflections observed with the metal-free compound and nickel phthalocyanine were consequently known to differ only by the contribution of the nickel atom, which geometrically had to be equal to the structure factor for nickel at the angle of reflection. A plot of the sums and differences of the observed *F* values for the two compounds against sin θ/λ showed a congregation of certain values about the theoretical curve of the nickel scattering factor. These values fixed the phase constants of the reflected rays, and therefore a Fourier synthesis could be formed directly from the measured *F* values.

FIG. 2.



Projection along the b *axis, showing one complete phthalocyanine molecule. The plane of the molecule is steeply inclined to the plane of the projection, the* M *direction making an angle of* 46° *with the* b *axis, and the* L *direction* 2·3°. *Each contour represents a density increment of one electron per* Å.², *the one-electron line being dotted.*

The Fourier synthesis of the (*h*0*l*) terms gave a projection of the structure on (010) which shows clearly resolved a pattern of atoms joined in six-membered and five-membered rings united together (see Fig. 2). This pattern may be said to provide the first purely physical demonstration of the truth of organic chemistry. It illustrates also the second condition necessary for the success of this determination of chemical structure—that the projection obtainable should be one in which little overlapping of atoms occurs, so that an unambiguous view may be obtained of the pattern as a whole. For example, the projection of the phthalocyanine structure along the *c* axis shows no clear resolution and could alone give no direct chemical information.

The method of direct determination of the phase constants of the Fourier terms by isomorphous replacement of metal atoms has already been used by J. M. Cork [2] and C. A. Beevers and H. Lipson [3] in their investigations of the alums. Owing to the peculiarly favourable chemical and crystal structure of the phthalocyanines the results are here much more striking, and it would seem worth while to explore further in the field of organic chemistry for other compounds which may possess this particular combination of characteristics. For most structures it will be necessary, of course, still to use the trial and error method—with the renewed confidence now given for its results.

The exact *X*-ray analyses discussed last year proved that the method was capable of giving purely chemical information of two kinds: (1) the actual determination of the mutual orientation of the atoms in the molecule, and here Robertson's analysis provides us with a notable advance; (2) the diagnosis of the nature of the chemical bonds present from the measured interatomic distances. In this both theory and experiment are still far from complete, but the function described by L. Pauling, L. O. Brockway, and J. Y. Beach [4] of the relation between bond length and single-bond–double-bond resonance does at least provide us with a new empirical standard with which to compare the experimental values.

Simple Molecular Compounds.

The crystal structures of most of the simplest quasi-spherical diatomic and triatomic molecules have already been measured, and the remaining types are likely to prove more complicated. E. Pohland [5] has found, for example, that solid hydrogen cyanide, nitric oxide, and sulphur dioxide are all doubly refracting. More complicated types of *X*-ray goniometer are needed for further work in the low-temperature region,[6] and with one of these W. H. Keesom and

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[2] *Phil. Mag.*, 1927, **4**, 688.

[3] *Proc. Roy. Soc.*, 1935, *A*, **148**, 664.

[4] *J. Amer. Chem. Soc.*, 1935, **57**, 2705.

[5] *Angew. Chem.*, 1936, **49**, 482.

[6] W. H. Keesom and K. W. Taconis, *Physica*, 1935, **2**, 463; R. L. McFarlan, *Rev. Sci. Instr.*, 1936, [ii], **7**, 82.

K. W. Taconis have studied γ-oxygen [7] and chlorine.[8] γ-Oxygen is cubic in agreement with the work of L. Vegard,[9] and chlorine crystallises at − 185° in the tetragonal system with eight (non-rotating) molecules in the unit cell. The Cl–Cl distance calculated from the rather limited *X*-ray intensities available is 1·99 in each molecule, and 2·79 A. between molecules. The lattice constant and *X*-ray intensities of solid hydrogen sulphide do not appear to change through a wide temperature range, though transitions, probably of rotation and orientation of the molecules, are indicated by other data, *e.g.*, dielectric constant.[10] That some orientation of the molecules does exist at liquid-air temperatures has been suggested to account for the Raman spectrum of the solid.[11]

In a number of crystals of this class, where rotating forms commonly occur, entropy calculations suggest that equilibrium is frequently not established at low temperatures. Tetramethylmethane has a zero-point entropy of 8 e.u. which may be due to random orientation,[12] and the residual entropy of ethane can similarly be correlated with a form of incomplete rotation.[13] The structure of ice is perhaps the most important example, since the difficulties of placing the hydrogen atoms in all varieties of ice so far measured have led many authors to describe the structures as ionic.[14] The Bernal–Fowler model [15] requires definite orientation of the hydrogen atoms between the water molecules forming hydrogen bonds, each hydrogen atom remaining still most closely associated with one oxygen, and although it is possible to form such a structure in a regular way, yet there is no evidence of any superstructure in the *X*-ray results. L. Pauling calculates that if the orientation is random, the residual entropy would be 0·805 e.u., compared with the observed value of 0·87 e.u.[16]

The structure of the different polymorphic forms of ice should be of particular interest for a further test of these theories. From time to time in the literature measurements have been reported suggesting that ordinary ice, ice-I, is rhombohedral, which might be due to a correctly oriented form of the Bernal–Fowler type. N. Seljakow [17] has, however, now shown that if distilled water is

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[7] *Physica*, 1936, **3**, 141.

[8] *Ibid.*, p. 237.

[9] *Z. Physik*, 1935, **98**, 1.

[10] E. Justi and H. Nitka, *Physikal. Z.*, 1936, **37**, 435.

[11] S. C. Sirkar and J. Gupta, *Indian J. Physics*, 1936, **10**, 227.

[12] J. G. Aston and G. H. Messerly, *J. Chem. Physics*, 1936, **4**, 391.

[13] J. D. Kemp and K. S. Pitzer, *ibid.*, p. 749.

[14] Cf. W. H. Barnes, *Trans. Roy. Soc. Canada*, 1935, [iii], **29**, III, 53.

[15] *J. Chem. Physics*, 1933, **1**, 515.

[16] *J. Amer. Chem. Soc.*, 1935, **57**, 2680.

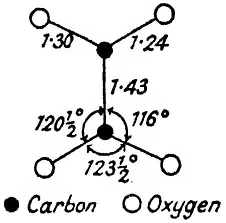
[17] *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **1**, 293; **2**, 227.

frozen from the surface in the open air, two quite different modifications may be obtained. Ordinary ice-I, α-ice, appears when the temperature of crystallisation is between 0° and − 8° and gives the usual hexagonal Laue photograph. Below − 8°, *i.e.*, with some degree of supercooling, β-ice is formed, which shows a quite different rhombohedral Laue pattern and appears to be pseudo-cubic ($c/a = 1{\cdot}33$).

The high-pressure forms of ice, ice-II [18] and ice-III,[19] according to R. L. McFarlan, have orthorhombic structures of some complication. Both the molecular arrangements suggested show oxygen atoms surrounded by four nearest neighbours at 2·71 A., very little different from the distance in ice-I, 2·74 A. The higher densities imposed by the higher pressure, 1·2 in ice-II, 1·105 in ice-III, are attained in both by different distortions from the regular tetrahedral arrangement of nearest neighbours shown by ice-I, which permits the next neighbour distance to decrease from 4·47 A. in ice-I to about 3·4 A. in ice-II and ice-III. It does not seem necessary to correlate this distortion with a truly ionic structure, since such alterations of the valency angle may occur under strain even with homopolar bonds such as those in diphenyl ether—where the C–O–C angle is about 128°.[20] In many hydrates the water molecules are surrounded by similarly distorted tetrahedra of oxygen atoms, and the most significant feature seems at present to be, not the distortion, but the even approximately tetrahedral nature of the co-ordination.

FIG. 3.

Dimensions of the Oxalic Acid Molecule.



Aliphatic Compounds.

To the complete structure determinations in the aliphatic series we may now add that of oxalic acid dihydrate by J. M. Robertson.[21] The approximate structure found by W. H. Zachariasen showed the two oxygen atoms to be differently situated with respect to the water molecules and suggested therefore that these were different in character. The results now obtained by the use of absolute intensities and double Fourier syntheses fully confirm and extend this. The two C–O distances are found to be different, 1·24 and 1·30 A., and though neither corresponds to pure double-bond or single-bond distances, they may be correlated with links mainly

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[18] *J. Chem. Physics*, **1936**, **4**, **60.**

[19] *Ibid.*, p. 253.

[20] L. E. Sutton and G. C. Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945.

[21] *J.*, **1936, 1817.**

C=O and C—OH respectively. The C–C distance as measured is considerably shorter than that first proposed, *viz.*, 1·43—1·45 A., which corresponds to 30—25% double-bond quality. According to calculations of J. E. Lennard-Jones,[22] such a shortening is to be expected in a single link between two doubly-bound carbon atoms, as, *e.g.*, in a conjugated chain. Here, it seems that it could take place through the co-operation of the water molecules forming hydrogen and hydroxyl bond chains through the structure as suggested by J. D. Bernal and (Miss) H. D. Megaw [23] (Type B).

Exactly opposite effects appear to occur with the oxalate ion, particularly in ammonium oxalate monohydrate.[24] Here the distance between the central carbon atoms is 1·58 A., longer than that expected for a normal single link. The lengthening might be due to repulsion between the negative parts of the CO_2 ions, and there certainly seems no allowance for a partial double-bond character of the central link. Also, the two CO_2 groups are found to be no longer coplanar, but inclined at an angle of about 28° to one another, a result which seems most reasonable if there is a pure single link at the centre, about which free rotation should be possible. In most other oxalates studied, *e.g.*, those of potassium, sodium, and rubidium, the ion is planar within a probable experimental error of ± 10°.[25] The difference in ammonium oxalate may partly be due to a new system set up by possible hydrogen-bond formation between the ammonium ions and oxygen atoms of the oxalate ion. The interatomic distances in ammonium and potassium oxalates show relations similar to those of ammonium azide compared with potassium azide[26] (see p. 210). Calcium oxalate dihydrate is tetragonal, and it is interesting that this occurs with calcium citrate in deposits at the bottom of the Weddell Sea.[27]

Investigations have begun on a number of the homologues of oxalic acid.[28] These crystallise commonly in two different polymorphic modifications, α and β, the α being the stable form for acids of more than nine carbon atoms, the β for those of less. The change is probably associated with the differential effective interaction of the carboxyl groups: below C_9 the crystals are hard and shining; above, platy and waxy. Of several tartaric acid derivatives described,[29] tartramide seems most promising for further exact

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[22] Private communication to J. M. Robertson.

[23] *Proc. Roy. Soc.*, 1935, *A*, **151**, 384.

[24] S. B. Hendricks and M. E. Jefferson, *J. Chem. Physics*, 1936, **4**, 102.

[25] S. B. Hendricks, *Z. Krist.*, 1935, **91**, 48.

[26] L. K. Frevel, *J. Amer. Chem. Soc.*, 1936, **58**, 779; *Z. Krist.*, 1936, **94**, 197.

[27] F. A. Bannister, *Discovery Reports*, 1936, XIII, 60.

[28] F. de la Tour, *Compt. rend.*, 1936, **202**, 1935.

[29] J. Wyart and Y. Ki-Heng, *ibid.*, **203**, 95.

information. A number of measurements are recorded on long-chain acids and salts,[30] and also the α-monoglycerides,[31] which have interesting liquid-crystal properties. The choleic acids are somewhat of a mystery, since the same *X*-ray photographs are obtained with considerable variation in fatty acid present.[32]

The measurements on oxalic acid and oxalates provide us with a series of C–O distances which can be described as due to varying single-bond–double-bond mixtures. That in metaldehyde probably represents the pure single link and is given as 1·43 ± 0·02 A.[33] Metaldehyde crystallises in the tetragonal system, each molecule having a fourfold axis of symmetry. The molecule consists of a puckered eight-membered ring of alternate oxygen and carbon atoms, similar to the six-membered ring of paraldehyde,[34] the methyl groups here lying approximately in the plane of the ring (Fig. 4). A Fourier projection along the four-fold axis has been obtained, but the parameters at right angles to this are not so accurately fixed.

FIG. 4.
Metaldehyde.

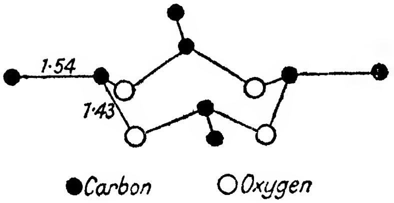
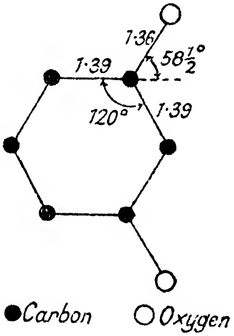


FIG. 5.
Resorcinol.



The whole series of C–O distances hitherto found in organic compounds, including that in resorcinol (p. 221), are shown in the table.

Main bond type.	Compound.	Interatomic distance, A.
C–O–C	Metaldehyde	1·43
*C–OH	Resorcinol	1·36
*C–OH	Oxalic acid dihydrate	1·30
$C–O^-$	Ammonium oxalate monohydrate	1·25
*C=O	Urea [35]	1·25
*C=O	Oxalic acid dihydrate	1·24
C=O	Benzoquinone [36]	1·14

* Probably most accurate values.

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[30] P. A. Thiessen and J. Stauff, *Z. physikal. Chem.*, 1936, **176**, 397; with W. Wittstadt, *Angew. Chem.*, 1936, **49**, 641; R. Brill, *ibid.*, p. 643.

[31] T. Malkin and M. R. el Shurbagy, *J.*, 1936, 1628.

Aromatic Compounds.

The exact structure of the molecule of resorcinol[37] is shown in Fig. 5. The most interesting feature of this crystal structure is the spiral method of packing, which is able to bring the hydroxyl groups within that distance of each other, *viz.* 2·66—2·74 A., associated with hydroxyl-bond formation without placing the carbon atoms nearer than the customary 3·5 A. Both theory and experiment now show that in the type of hydrogen- and hydroxyl-bond formation common in organic compounds there is not usually complete degeneracy, hydroxyl and keto-groups still preserving individual characteristics. This is true in oxalic acid (above) and also, apparently, in quinhydrone, where more exact work shows that the symmetry first found is a pseudo-symmetry, and that the benzoquinone and the quinol molecules can actually be distinguished in the crystal cell.[38] Their mutual arrangement is necessarily almost exactly the same as that first put forward, and the lines of attraction between them are still those of the C⁚O . . . HO bonds running through the whole structure. In isatin, the question of a difference of this kind is bound up with the old problem of a distinction between the lactim and the lactam structure. E. G. Cox, T. H. Goodwin, and (Miss) A. I. Wagstaff[39] find an orientation of the molecules in the crystal unit which indicates a hydrogen bond between the nitrogen atom and the carbonyl group of neighbouring molecules; but whether this is to be written mainly as of the type NH . . . O⁚C (lactam) or =N . . . HOC (lactim), only a complete analysis can decide. The present work implies that to a certain degree the structure is intermediate between the two.

In the phthalocyanine molecule there appears to be the first example of an internal hydrogen bond. The exact molecular structure found (see p. 215) is illustrated in Fig. 6. The direct Fourier projection first obtained showed that the ring system is somewhat inclined to the plane of projection, but the regularity of the pattern proves that the molecule is essentially planar. The angle of inclination adopted agrees with the observed intensities.

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[32] Y. Go and O. Kratky, *Z. Krist.*, 1936, **92**, 310.

[33] L. Pauling and D. C. Carpenter, *J. Amer. Chem. Soc.*, 1936, **58**, 1274.

[34] D. C. Carpenter and L. O. Brockway, *ibid.*, p. 1270; P. G. Ackermann and J. E. Mayer, *J. Chem. Physics*, 1936, **4**, 377.

[35] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, 1934, **89**, 462.

[36] J. M. Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106.

[37] *Idem, ibid.*, 1936, *A*, **157**, 79; cf. (Mrs.) K. Lonsdale, *Nature*, 1936, **137**, 826.

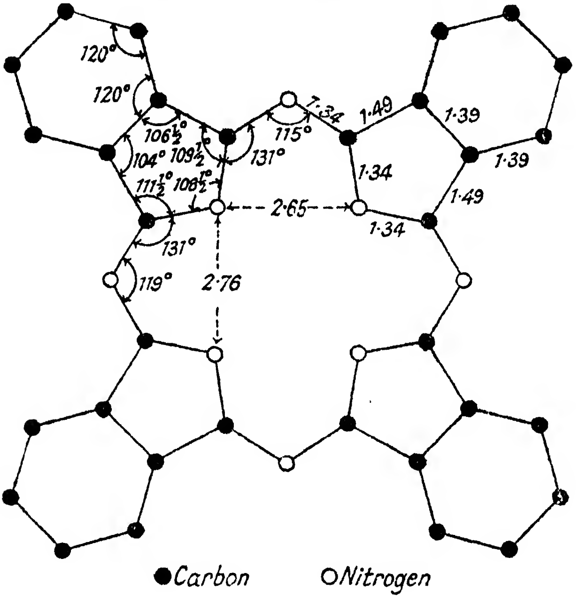
[38] J. Palacios and O. R. Foz, *Anal. Fis. Quim.*, 1935, **33**, 627; J. Bijvoet, private communication.

[39] *Proc. Roy. Soc.*, 1936, *A*, **157**, 399.

Chemically the structure is that assigned by R. P. Linstead,[40] but the interatomic distances indicate the additional regularity of a complete resonance system. There are no systematic differences, *e.g.*, in the C–C distances of the benzene ring that might indicate either *o*-quinonoid forms or fixation of one of the Kekulé modes by the fusion of the five-membered ring; but the molecule as a whole shows a slight departure from tetragonal symmetry, the central nitrogen atoms being drawn more closely together along two out of the four possible lines. The distance between them, *viz.*, 2·65 A., suggests that this is due to hydrogen-bond formation and the hypothesis is being tested by further examination of the metallic derivatives.[41]

Fig. 6.

Dimensions of the Phthalocyanine Molecule.



It is comparatively rarely that the full symmetry of a molecule is shown in that of the crystal if the symmetry is at all high. In the phthalocyanines this is due to the molecules being packed with the planes of neighbouring ring systems slanting at a considerable angle to one another; and this behaviour appears to be common among the many aromatic compounds of which preliminary measurements

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[40] See *Ann. Reports*, 1935, **32**, 360.

[41] J. M. Robertson, *J.*, **1936**, 1736.

are recorded this year[42] and also in reduced ring systems such as those of the sex hormones.[43] One exception is hexabromomethylbenzene which crystallises in a very simple rhombohedral structure with one molecule in the unit cell.[44] This molecule must crystallographically possess a three-fold axis of symmetry, and the near identity of the intensities of equatorial and layer-line reflections shows that all the atoms fall nearly into a single plane. A planar character is shown also in the crystal structure of hexaethylbenzene,[45] which is, however, triclinic like hexamethylbenzene. Molecular centres of symmetry can more readily appear than axes, *e.g.*, in dibenzanthracene,[46] rubrene,[47] and quaterphenyl.[48] In the optically active substituted diphenyls[48] the crystal centre of symmetry disappears, as would be expected.

The exact analyses described show several examples of slight distortions of the external valency angles of the benzene carbon atoms towards substituent atoms. That in resorcinol is very small and may not be real, and that in the phthalocyanines is forced by the fusion of the five-membered ring. Both these distortions are in the plane of the ring, but in two other structures examined, *p*-toluidine[49] and fluorene,[50] preliminary calculations of intensities suggest that deviations also occur at right angles to this plane. In fluorene, however, where such a distortion would seem most plausible, the dipole moment of the solution indicates a planar structure,[51] and it is evident that further work is necessary to establish with certainty the correct configuration in the solid.

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[42] J. Iball, *Z. Krist.*, 1936, **92**, 293; **93**, 47; **94**, 7; **95**, 282; J. Dhar and A. C. Guha, *ibid.*, 1935, **91**, 123; M. Milone, *ibid.*, 1936, **93**, 113; M. Prasad and J. Shanker, *J. Indian Chem. Soc.*, 1936, **13**, 123; with M. P. Lakhani, *ibid.*, p. 519; R. Hultgren, *J. Chem. Physics*, 1936, **4**, 84; E. Hertel and H. W. Bergk, *Z. physikal. Chem.*, 1936, *B*, **33**, 319; L. Rivoir and R. Salvia, *Anal. Fis. Quim.*, 1935, **33**, 314; B. K. Blount and (Miss) D. Crowfoot, *J.*, 1936, 414; J. M. Robertson, M. Prasad, and (Miss) I. Woodward, *Proc. Roy. Soc.*, 1936, *A*, **154**, 187.

[43] J. D. Bernal and (Miss) D. Crowfoot, *Z. Krist.*, 1936, **93**, 464.

[44] H. S. Backer, *Rec. trav. chim.*, 1935, **54**, 745; J. Beintema, P. Terpstra, and W. J. van Weeden, *ibid.*, p. 962.

[45] H. K. Pal and A. C. Guha, *Z. Krist.*, 1936, **92**, 392; N. Ganguli, *ibid.*, **93**, 42.

[46] J. Iball, *Nature*, 1936, **137**, 361.

[47] W. H. Taylor, *Z. Krist.*, 1936, **93**, 151; cf. E. Bergmann and E. Herlinger, *J. Chem. Physics*, 1936, **4**, 532.

[48] L. W. Pickett, *J. Amer. Chem. Soc.*, 1936, **58**, 2299.

[49] J. Wyart, *Bull. Soc. franç. Min.*, 1935, **58**, 281.

[50] J. Iball, *Z. Krist.*, 1936, **94**, 397; J. W. Cook and J. Iball, *Chem. and Ind.*, 1936, 467.

[51] E. D. Hughes, (Mrs.) C. G. Le Fèvre, and R. J. W. Le Fèvre, *ibid.*, pp. 545, 581.

Fibre Structures.

The most important contribution of the first application of X-ray crystallography to the problem of fibre structures was the demonstration that the patterns obtained corresponded to units within the molecule many times smaller than the estimated molecular size.[52] Most subsequent work has concentrated on the examination of these small repeating units, and with the introduction of such methods of analysis of fibre diagrams as that proposed by E. Sauter this year,[53] it is to be hoped that still more accurate information will be made available along this line. With synthetic polymers, however, such as the polyoxymethylenes, two types of X-ray interference can be obtained, one due to the fibre repeat unit and the other to small angle reflections corresponding to the molecular length.[54] Most natural polymers have very much larger molecules than these, and long spacings due to regularity in chain length would be much more difficult to observe; but the constant reports of long spacings in the literature—particularly on proteins [55]—suggest that a more comprehensive search should be made in the region of small angle scattering. This has been now initiated by R. W. G. Wyckoff and R. B. Corey, using for their first attempt apparatus capable of showing spacings up to 150 A.[55a] They find that, on the basis of the scattering visible at small angles, the compounds examined fall into three classes, of which rubber, cellulose, and the proteins may be taken as typical.

For stretched rubber, Wyckoff finds no scattering at all at small angles, which is not surprising since, even if chains of a single length were present, it would be unlikely that the orientation produced by stretching would be sufficient to demonstrate them. However, in β-rubber, in which a rather different configuration of the chain appears, a spacing of 115 A., 24 times the simple identity period, has been observed.[56] This may, of course, represent no more than a purely crystallographic superstructure. The exact configuration of the residues in ordinary, "crystalline," α-rubber has been reinvestigated by K. H. Meyer and W. Lotmar,[57] who find a monoclinic cell in which the chains themselves have a twofold

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[52] Cf. J. R. Katz, *Trans. Faraday Soc.*, 1936, **32**, 77.

[53] *Z. Krist.*, 1936, **93**, 93.

[54] H. Staudinger, H. Johner, R. Signer, G. Mie and J. Hengstenberg, *Z. physikal. Chem.*, 1927, **126**, 425.

[55] See *Ann. Reports*, 1935, **32**, 241; W. T. Astbury, *Nature*, 1936, **137**, 803.

[55a] *J. Biol. Chem.*, 1936, **114**, 407.

[56] G. W. Pankow, *Helv. Chim. Acta*, 1936, **19**, 221.

[57] *Sitzungsber. Akad. Wiss. Wien*, 1936, IIb, **145**, 721; *Arch. Sci. phys. nat.*, 1936, [v], **18**, Suppl., 61.

screw axis of symmetry, the crystal being essentially a racemate of right- and left-screwed molecules. The density found is still rather lower than that calculated for the measured unit, but it seems probable that this is due to holes between the rubber crystallites. The same discrepancy appears with the "inorganic" rubber, phosphonitrile chloride.[58] In this, too, the crystal structure suggests long chains formed on a screw-axis pattern, the space group here being orthorhombic. Both rubber and phosphonitrile chloride give very similar *X*-ray scattering curves in the amorphous state. That of rubber has now been submitted to a Fourier analysis, and the radial density found is in good agreement with the configuration of the rubber chain suggested for α-rubber.[59] The strongest peak at 5 A. corresponds to distances between neighbouring chains and moves out to 6·15 A. in phosphonitrile chloride. In thin rubber films the α-rubber structure again appears, but may be rather differently oriented on stretching.[60]

Cellulose, according to Wyckoff, shows diffuse scattering at small angles but no definite line pattern. This is contrary to many previous reports of long spacings, but some at least of these have been proved by W. A. Sisson, G. L. Clark, and E. A. Parker [61] to be actually not diffraction lines but absorption edges, and results might differ with cellulose from different sources. G. L. Clark and A. F. Smith [62] have also investigated chitin and various derivatives such as its nitrate and chitosan, with which, again, long spacings seem to appear. For the repeat structure of chitin, their results agree with those of K. H. Meyer and G. W. Pankow,[63] the unit cell being similar in dimensions to that of cellulose, and larger than that put forward by A. N. J. Heyn; [64] but the latter's work does show the orientation of the chitin chains in the sporangiophore of the fungus *phycomyces*. It is interesting that plant and animal chitin appear identical,[65] whereas among the starches from these two sources there are marked differences. Glycogen has been made to give only a single amorphous ring, and the patterns from several vegetable starches show a number of Debye lines and differ from

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[58] K. H. Meyer, W. Lotmar, and G. W. Pankow, *Helv. Chim. Acta*, 1936, **19**, 930; K. H. Meyer and G. W. Pankow, *Arch. Sci. phys. nat.*, 1935, [v], **17**, 139.

[59] G. L. Simard and B. E. Warren, *J. Amer. Chem. Soc.*, 1936, **58**, 507.

[60] K. I. Krilov, *Physikal. Z. Sovietunion*, 1935, **8**, 136.

[61] *J. Amer. Chem. Soc.*, 1936, **58**, 1635.

[62] *J. Physical Chem.*, 1936, **40**, 863.

[63] *Helv. Chim. Acta*, 1935, **18**, 589.

[64] *Proc. K. Akad. Wetensch. Amsterdam*, 1936, **39**, 132.

[65] K. H. Meyer and W. Lotmar, *Arch. Sci. phys. nat.*, 1935, [v], **17**, 287; with G. van Iterson, *Rec. trav. chim.*, 1936, **55**, 61.

plant to plant.[66] The actual laying down of these fibres in plants is a fascinating problem.[67] In *Valonia*, protoplasm streams can be observed running nearly at right angles to the primary cellulose fibre axis,[68] and these probably determine the orientation of the secondary axis as found by *X*-ray studies. Perhaps the time is not far off when *X*-ray cinematographs will be taken of this process. They have already been successfully made by M. Mathieu for the nitration of cellulose,[69] and could obviously be applied widely, especially in the many other cellulose reactions awaiting elucidation.[70] In the nitration of cellulose with gaseous nitrogen pentoxide, the whole process can be observed in the course of one hour from the first disappearance of regularity in the direction of the cellulose fibre axis to the final appearance of the new fibre period, 25·1 A., of trinitrocellulose.

In the third group, the proteins, more and more evidence appears of a surprising degree of natural orientation and complexity of structure.[71] The only natural protein fibre to show an almost amorphous state appears to be " byssus " or silk of oysters, which may be a mixture of different chains.[72] In most cases the α-keratin oriented state appears even in the actual arrangement of the protein in cell walls,[73] *e.g.*, of wool cells, [74] and the structures present may be much more complicated than this, as the patterns obtained from tendon, collagen, quill, and feather keratin show.[55] In all these, spacings over 100 A. long have been observed, and the real fibre repeat of tendon is probably at least 330 A. Truly crystalline Debye–Scherrer patterns are given by both the Bence Jones protein [75] and chymotrypsinogen [55] suspended in water, but the most interesting results of all have been obtained on the tobacco mosaic virus. The preparation of biologically active crystals was first effected by

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[66] F. May and L. Graf, *Z. Biol.*, 1936, **97**, 167.

[67] W. Wergin, *Angew. Chem.*, 1936, **49**, 843; W. A. Sisson, *J. Physical Chem.*, 1936, **40**, 343; W. K. Farr, *Paper Trade J.*, 1935, **101**, T.A.P.P. I. Sect. 183; F. Worschitz, *Magyar Chem. Fol.*, 1934, **40**, 60; T. Fujiwara and Y. Imanaka, *J. Sci. Hiroshima Univ.*, 1936, *A*, **6**, 237.

[68] G. van Iterson, *Nature*, 1936, **138**, 365.

[69] *Ibid.*, p. 824.

[70] M. Mathieu and (Mdlle.) T. Petitpas, *Compt. rend.*, 1936, **202**, 46; A. J. Barry, F. C. Peterson, and A. J. King, *J. Amer. Chem. Soc.*, 1936, **58**, 333; K. Hess and C. Trogus, *Z. Elektrochem.*, 1936, **42**, 696, 705, 710; J. B. Calkin, *J. Physical Chem.*, 1936, **40**, 27; G. Natta and M. Baccaredda, *Atti R. Accad. Lincei*, 1936, [vi], **23**, 444; M. Isihara, *J. Soc. Chem. Ind. Japan*, 1936, **39**, 62, 65, 68, 70; A. Frey-Wyssling, *Helv. Chim. Acta*, 1936, **19**, 901.

[71] Cf. W. T. Astbury, *Nature*, 1936, **137**, 803.

[72] G. Centola, *Gazzetta*, 1936, **66**, 71.

[73] A. Giroud and G. Champetier, *Bull. Soc. Chim. biol.*, 1936, **18**, 656.

[74] H. J. Woods, *Proc. Leeds Phil. Soc.*, 1935—36, **3**, 132.

[75] A. Magnus-Levy, K. H. Meyer, and W. Lotmar, *Nature*, 1936, **137**, 616.

W. M. Stanley,[76] and the Debye–Scherrer pattern obtained from a suspension of these by R. W. G. Wyckoff [77] and R. B. Corey is similar to, though somewhat more complicated than, those of other crystalline proteins. This is true both of preparations obtained by the usual methods of protein fractionation and of " crystalline " pellets isolated directly by centrifuging clear juice pressed from virus-infected plants.[78] The most remarkable effects are shown by the highly purified protein solutions prepared by F. C. Bawden and N. W. Pirie.[79] These separate on standing into two layers; the lower layer, which may be water-clear, is liquid-crystalline, whereas the upper layer shows to a high degree the phenomenon of anisotropy of flow. On drying, at first a " wet gel " is formed with a much higher birefringence than the liquid but this gradually shrinks by about 50% to form a " dry " gel. J. D. Bernal and I. Fankuchen [79] have obtained *X*-ray patterns both from the wet and the dry gel, and from the liquid down to 13% concentration oriented by flow. All show approximately the same large angle scattering, which can be correlated with that given by the crystals —a protein pattern of some complexity with a repeat unit of 3 × 22·2 A. This must be due to the internal structure of the protein molecule. There is also an inner pattern corresponding to a hexagonal packing of long rods; and the unit of the long spacing here varies from 131·8 A. in the dried gel to 398 A. in the liquid, and corresponds to distances between the protein molecules. The relations between the various patterns permit Bernal and Fankuchen to deduce the presence of rods 100 A. across roughly triangular in section. Both the sharpness of the *X*-ray reflections and the shape of the lenticels formed in the liquids suggest a length for these rods of at least 1000 A., which would agree with Svedberg's molecular weight of about 17,000,000; [80] but there is no *X*-ray evidence at present against the rods being quite indefinite in length. Crystallographically, the gel and the liquid structures may be assigned to C. Hermann's liquid-crystal class R D RD,[81] there being regularity within the long rods and in their arrangements normal to their length without accurate co-ordination between the two; but the observation of such regularities is indeed an achievement in a molecule of such a high molecular weight and with at least a suspicion of life.

D. M. C.

E. G. Cox.
D. M. Crowfoot.

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[76] *Science*, 1935, **81**, 644; *J. Biol. Chem.*, 1936, **115**, 673.

[77] *Ibid.*, **116**, 51.

[78] *Science*, 1936, **84**, 513.

[79] *Nature*, 1936, **138**, 1051.

[80] *J. Amer. Chem. Soc.*, 1936, **58**, 1863.

[81] *Z. Krist.*, 1931, **79**, 186.

ORGANIC CHEMISTRY.

1. STEREOCHEMISTRY.

Deutero-compounds.—A number of attempts have been made to ascertain if a compound CHDRR′ could exhibit optical activity owing to the difference between hydrogen and deuterium. H. Erlenmeyer and H. Gärtner[1] failed to resolve a partly deuterated β-phenylpropionic acid, $C_6H_{2.18}D_{2.82}\cdot C_2H_{1.62}D_{2.38}\cdot CO_2H$, and later[2] phenylpentadeuterophenylacetic acid, $C_6D_5\cdot CHPh\cdot CO_2H$. E. Biilman, K. A. Jensen, and E. Knuth[3] at first concluded that decomposition of *l*-bornylmagnesium chloride with deuterium oxide gave a slightly active 2-deuterocamphane, but repetition[4] of this work showed that water and deuterium oxide gave products which were stereochemically indistinguishable. M. T. Leffler and R. Adams[5] reduced *l*-bornylene with hydrogen and with deuterium, and found that, although 2 : 3-dideuterocamphane had a higher density than camphane, it had the same optical rotation as the latter. The same authors[6] also reduced ethyl maleate and ethyl fumarate catalytically with deuterium, and obtained from both the same ethyl αα′-dideuterosuccinate, and this was found to be saponified to a single acid, the alkaloid salts of which showed no mutarotation. Similarly, J. B. M. Coppock and S. M. Partridge[7] reduced γ-phenyl-α-methylallyl alcohol with hydrogen and with deuterium, and failed to observe any optical difference between the products. All the above authors concluded, therefore, that the formally " asymmetric " carbon atom in CHDRR′ does not give rise to optical activity.[8]

On the other hand, G. R. Clemo and A. McQuillen[9] have claimed the resolution of pentadeuterobenzhydrylamine, $C_6D_5\cdot CHPh\cdot NH_2$, prepared by reducing the oxime of pentadeuterobenzophenone, obtained by a Friedel–Crafts reaction from hexadeuterobenzene. The *d*- and the *l*-hydrogen tartrate of the base were described as

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[1] *Helv. Chim. Acta*, 1936, **19**, 145, 331.

[2] *Ibid.*, *p.* 1169.

[3] *Ber.*, 1936, **69**, 1031.

[4] E. Biilmann, K. A. Jensen, and B. Bak, *Ber.*, 1936, **69**, 1947.

[5] *J. Amer. Chem. Soc.*, 1936, **58**, 1555.

[6] *Ibid.*, p. 1551.

[7] *Nature*, 1936, **137**, 907.

[8] Compare also R. Schoenheimer and co-workers, *J. Biol. Chem.*, 1935, **111**, 163, 169, 175, 183.

[9] *J.*, 1936, 808.

having $[\alpha]_D \pm 13{\cdot}2°$ (solvent not stated), but the observed angles recorded for the two antimeric bases were only $+ 0{\cdot}041°$ and $- 0{\cdot}136°$, leading to $[\alpha]_D^{16°} + 5{\cdot}0°$ and $- 5{\cdot}7°$, respectively. The hexadeuterobenzene used in this work appears to have had a freezing point of $- 1{\cdot}0°$ approximately,[10] whereas the pure substance [11] melts at $+ 6{\cdot}8°$, and the resolution thus becomes inconclusive, from the point of view of deciding whether the undoubted activity was due to the difference between hydrogen and deuterium. It seems improbable that this difference could ever give rise to pronounced dissymmetry. The preparation and resolution of such a compound as $C_6D_5{\cdot}CHMe{\cdot}OH$, and comparison of the specific rotation with that of phenylmethylcarbinol, would make a useful contribution to the subject.

In this connexion, it may be noted that H. Erlenmeyer and H. Schenkel [12] have crystallised *l*-mandelic and *d*-atrolactic acid from water and from deuterium oxide, the second crystallisation causing partial replacement of hydrogen by deuterium to give the compounds $OD{\cdot}CHPh{\cdot}CQ_2D$ and $OD{\cdot}CPhMe{\cdot}CO_2D$, respectively. Determination of $[\alpha]_D$ in acetophenone solution gave the following results :

		$[\alpha]_D^{H_2O}/[\alpha]_D^{D_2O}$.
Mandelic acid *ex* water....................	$-179{\cdot}10° \pm 0{\cdot}13°$	1·046
ex D_2O	$-173{\cdot}27 \pm 0{\cdot}13$	
Atrolactic acid *ex* water	$+ 37{\cdot}98 \pm 0{\cdot}1$	1·032
ex D_2O	$+ 36{\cdot}79 \pm 0{\cdot}1$	

In a previous paper with A. Epprecht,[13] the same authors described the replacement, in *l*-mandelic acid, of hydrogen by deuterium under two sets of conditions, one in which racemisation is excluded and one in which it goes to completion (51 hours at 140° in a closed vessel). In both instances the same two hydrogen atoms are replaced by deuterium, and it is concluded that enolisation is not a *necessary* intermediate stage in racemisation, even in presence of alkali, although here it is one of two alternative simultaneous processes. The explanation of F. Hund,[14] based on quantum mechanics, is preferred.

Optically Active Allene Hydrocarbon.—The resolution of an allene hydrocarbon by P. Maitland and W. H. Mills was reported last year.[15] Full details of this work have now been published.[16] The

[10] *Idem, J.*, 1935, 851.

[11] H. Erlenmeyer, H. Lobeck, H. Gärtner, and A. Epprecht, *Helv. Chim. Acta*, 1936, **19**, 336; C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J.*, 1936, 915.

[12] *Helv. Chim. Acta*, 1936, **19**, 1199.

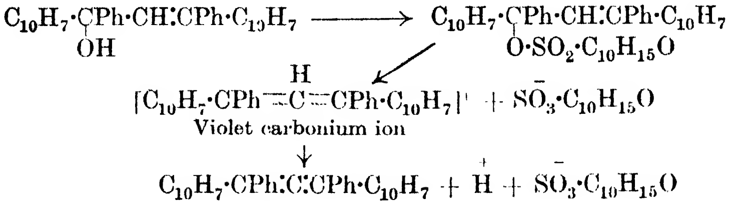
[13] *Ibid.* p. 1053.

[14] *Z. Physik*, 1927, **43**, 805.

[15] *Ann. Reports*, 1935, **32**, 243.

[16] *J.*, 1936, 987.

mechanism of the dehydration of αγ-diphenyl-αγ-di-1-naphthylallyl alcohol by *d* (or *l*)-camphorsulphonic acid, resulting in the formation of unequal amounts of *d*- and *l*-diphenyldinaphthylallene, is given as follows:



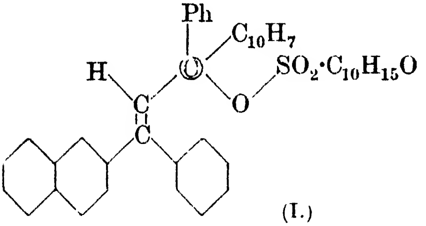
$$C_{10}H_7\cdot\underset{OH}{CPh}\cdot CH{:}CPh\cdot C_{10}H_7 \longrightarrow C_{10}H_7\cdot\underset{O\cdot SO_2\cdot C_{10}H_{15}O}{CPh}\cdot CH{:}CPh\cdot C_{10}H_7$$

$$[C_{10}H_7\cdot CPh \overset{H}{=} C = CPh\cdot C_{10}H_7]^+ + \overset{-}{SO_3}\cdot C_{10}H_{15}O$$

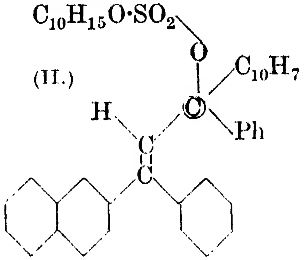
Violet carbonium ion

$$C_{10}H_7\cdot CPh{:}C{:}CPh\cdot C_{10}H_7 + \overset{+}{H} + \overset{-}{SO_3}\cdot C_{10}H_{15}O$$

It is pointed out that the configuration of the ester necessary for *trans*-elimination of camphorsulphonic acid is (I), in which the camphorsulphonate group is surrounded by three rigid and large aromatic groups, which have restricted powers of movement. This results in close definition of the position of the camphorsulphonate group, and the dissymmetry of this group must cause its relationship to its immediate environment in the molecule to be considerably affected by an interchange of the phenyl and the naphthyl group on the asymmetric carbon atom. The rate of *trans*-elimination should therefore be greater in one of the antimeric forms of the alcohol than in the other. In the configuration (II) necessary for *cis*-elimination, the camphorsulphonate group is far less sterically enveloped, and therefore an interchange of phenyl and naphthyl groups would be much less likely to cause an appreciable difference in the rate of elimination of the camphorsulphonate ion. The optically active allene possesses great optical stability, being little affected after nine hours' heating in decalin solution at 190°.



(I.)



(II.)

Dissymmetry of Phenoxarsines.—A third example of optical activity in the phenoxarsine series has been provided.[17] 10-Phenylphenoxarsine-2-carboxylic acid possesses high optical stability, but oxidation of ·As· in an active specimen to ·AsO· was accompanied by loss

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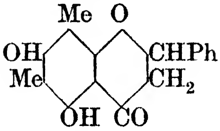
[17] (Miss) M. S. Lesslie and E. E. Turner, *J.*, 1936, 730.

of activity, although the oxide contains an "asymmetric arsenic atom."

Optically Active Flavanone.—In continuation of previous work,[18] *dl*-demethoxymatteucinol (III) has been resolved[19] by means of *l*-menthoxyacetyl chloride.[20] 7-Hydroxyflavanone also was resolved by a similar method. It is suggested that, although flavanones

(III.)



capable of being optically active are usually found to be inactive when isolated from plants, this is due to racemisation during removal of the sugar residue from the glucoside. If natural *l*-demethoxymatteucinol, having $[\alpha]_D - 50{\cdot}0°$, is converted into its *l*-menthoxyacetate and the latter is saponified, the recovered flavanone has only $[\alpha]_D - 32{\cdot}1°$.

Geometrical Isomerism.—G. Heller[21] concludes that the published work[22] of A. Binz and K. Schädel indicates the possibility of indigotin assuming the *cis*-form on the fibre of dyed materials, its reactions being different under these conditions from those obtainable with the free substance, which is admittedly the *trans*-form.[23]

The work of O. L. Brady and F. P. Dunn[24] suggested that the inter-conversion of α- and β-oximes by means of concentrated hydrochloric acid led to an equilibrium. W. Theilacker and L-H. Chou[25] now find that this is true for the 2 : 6-dichloro-3-nitrobenzaldoximes. Treatment of either the α- or the β-form with concentrated hydrochloric acid produces a mixture containing 75—76% of the β-oxime. On the other hand, T. S. Patterson and his co-workers[26] concluded that the change produced only one of the two forms. Patterson's method of investigation depends on the fact that when α- and β- (optically inactive) oximes are dissolved in an optically active solvent, they influence the specific rotation of the latter to different extents, so that any stereoisomeric change can be followed polarimetrically. Theilacker and Chou have now studied the α- and

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[18] *Ann. Reports*, 1934, **31**, 256.

[19] S. Fujise and A. Nagasaki, *Ber.*, 1936, **69**, 1893.

[20] A. E. Knauf, P. R. Shildneck, and R. Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 2109.

[21] *Ber.*, 1936, **69**, 563.

[22] *Ber.*, 1912, **45**, 586.

[23] I. Posner, *Ber.*, 1926, **59**, 1799.

[24] *J.*, 1913, **103**, 1621.

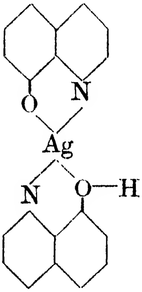
[25] *Annalen*, 1936, **523**, 143.

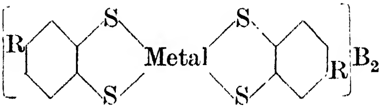
[26] *J.*, 1907, **91**, 504; *Ber.*, 1907, **40**, 2564; *J.*, 1912, **101**, 26, 2100; 1929, 1895.

β-anisaldoximes by the Brady–Dunn method (mixed melting point curve) and shown that in this case also an equilibrium exists. A solution of either the α- or the β-oxime in ethyl *d*-tartrate contained, after equilibration, 7% of β- and 93% of α-oxime.

Optically Active Metal Complexes.—F. Hein and H. Regler[27] have obtained a complex silver salt (IV), the *d*-α-bromocamphor-π-sulphonate of which could be separated into fractions having $[\alpha]_D^{19°}$ from + 37·4 ± 0·5° to + 47·8 ± 0·5°. Removal of the sulphonate left an inactive base, but the results are regarded as indicating that in these compounds the valencies of the silver atom are tetrahedrally disposed. Silver complexes of 8-hydroxyquinoline have also been investigated by Y. Nakatsuka.[28]

(IV.)





(V.)

W. H. Mills and R. E. D. Clark[29] have prepared *spirocyclic* derivatives of the type (V), in which R is methyl or chlorine, the metal is mercury, cadmium or zinc, and B may be a univalent metal or alkaloid + hydrogen. The quinine salt of the mercury complex (R = Cl), when prepared by heating equimolecular quantities of *l*-chlorobenzene-3 : 4-dithiol and quinine in chloroform solution with mercuric oxide, is obtained as an α-form, sparingly soluble in chloroform, but soluble in acetone. The acetone solution soon deposits a β-form, which is soluble in chloroform, but the solution so obtained rapidly becomes a jelly, owing to the separation of the α-form. It was concluded that the α- and the β-form are the two possible diastereoisomerides, *l*B*d*A and *l*B*l*A, but in spite of the use of an apparatus specially designed to permit of the polarimetric examination of a substance within about twenty seconds of its being brought into solution, no mutarotation could be detected at temperatures as low as — 35°.

Optical Activity in Relation to Tautomeric Change.—In 1933, C. K. Ingold and C. L. Wilson[30] began a series of investigations in

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[27] *Ber.*, 1936, **69**, 1692; see also this vol., p. 163.

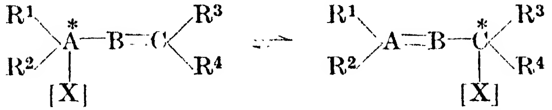
[28] *Bull. Chem. Soc. Japan*, 1936, **11**, 45.

[29] *J.*, 1936, 175.

[30] *J.*, 1933, 1494.

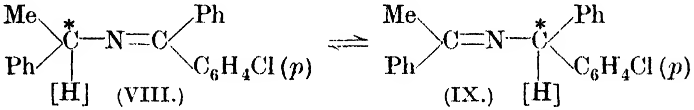
order to see if optical activity survived such a change as that of (VI) ⇌ (VII) :

(VI.)



(VII.)

The only example then known[31] of an isomeric change involving movement of the single centre of asymmetry responsible for optical activity was the conversion of linalyl acetate or formate into the corresponding optically active α-terpinyl ester. This change is, however, more complex than, and of a different type from, that generalised above, and specifically investigated with the pair (VIII) ⇌ (IX) :



(VIII.) (IX.)

The change (VIII) ⇌ (IX) is promoted by sodium ethoxide in alcoholic solution, and was studied with inactive and with active (VIII). The second set of experiments led to inactive (IX).

Later,[32] the same authors measured the velocity of racemisation of (VIII) and also its speed of tautomeric change and the corresponding equilibrium constants. It was found that the velocity of racemisation was not measurably different from the rate of isomerisation, the two rates being measurable, of course, by independent methods. Racemisation could have occurred in two ways. In the first, optical activity could have been retained in the intermediate ions, and lost on formation of (IX). In the second, optical activity could have been lost in the ions. The second alternative is shown to involve assumptions of unlikely coincidental disturbing factors, and it therefore appeared to follow that mesomeric ions generally should be able to retain at any rate some of the optical activity of the compound giving rise to them. In the bromination of an optically active ketone[33] the mesomeric keto-enol anion can similarly retain optical activity whilst being attacked by the bromine. An example of this kind was studied by Ingold and Wilson,[34] who brominated 2-*o*-carboxybenzylindan-1-one[35] (X). Again the rates of racemisation and bromination were found to be the same. Later, a return was made[36] to the

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[31] I. Stephan, *J. pr. Chem.*, 1898, **58**, 109; O. Zeitschel, *Ber.*, 1906, **39**, 1780.

[32] *J.*, 1934, 93.

[33] H. Leuchs and J. Wutke, *Ber.*, 1913, **46**, 2420.

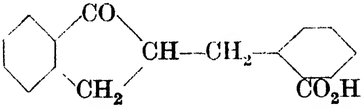
[34] *J.*, 1934, 773.

[35] H. Leuchs and D. Radulescu, *Ber.*, 1912, **45**, 189; 1913, **46**, 2420.

[36] S. K. Hsü, C. K. Ingold, and C. L. Wilson, *J.*, 1935, 1778.

azomethines, in order to deal with the coincidental factors referred to above [*e.g.*, that all the intermediate ion passes into (IX) and

(X.)



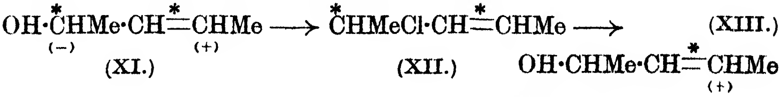
does not re-form (VIII)]. Two new examples were chosen :

$$\mathrm{CHPhMe{\cdot}N{:}CPh_2} \rightleftharpoons \mathrm{CPhMe{:}N{\cdot}CHPh_2} \text{ and}$$
$$(p)\mathrm{Ph{\cdot}C_6H_4{\cdot}CHPh{\cdot}N{:}CHPh} \rightleftharpoons (p)\mathrm{Ph{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}CH_2Ph}$$

The results obtained confirmed those of previous observations, and it was thus established that, if the seat of dissociation of the proton is asymmetric, then the intermediate mesomeric anion is optically stable. On the other hand, from their experimental work, the authors conclude, in agreement with the requirements of the quantum mechanics of the mesomeric effect, that the intermediate anion never becomes kinetically free. It is thought that a modification of T. M. Lowry's view[37] of the mechanism of prototropy is nearer the truth than the view of C. K. Ingold, C. W. Shoppee, and J. F. Thorpe.[38]

R. H. Kimball[39] has made simultaneous measurements of the rate of racemisation and of enolisation of *l*-menthyl α-phenylacetoacetate, in presence of piperidine as a catalyst : $\mathrm{CH_3{\cdot}CO{\cdot}CHPh{\cdot}CO_2C_{10}H_{19}} \rightleftharpoons \mathrm{CH_3{\cdot}C(OH){:}CPh{\cdot}CO_2C_{10}H_{19}}$. Racemisation is much quicker than enolisation, which therefore involves an intermediate stage, in which nearly two-thirds of the racemisation occurs, only one-third involving actual transformation to the enol form. Two explanations are offered : (1) that asymmetry is lost at an intermediate anion stage and (2) that there is reversible formation of a small amount of open-chain enol, followed by a slower accumulation of chelated enol. The anion passes into the keto-form twice as fast as it does into the enol form, that is, the keto-form ionises more rapidly than the enol form, owing to chelation of the latter, with consequent restriction of proton mobility.

Asymmetric Synthesis.—H. W. J. Hills, J. Kenyon, and H. Phillips[40] found that (−) αγ-dimethylallyl alcohol (XI) was converted by phosphorus trichloride into (+) αγ-dimethylallyl chloride (XII), the latter being hydrolysed by a cold aqueous suspension of calcium carbonate to a dextrorotatory form (XIII) (?) :



$$\mathrm{OH{\cdot}}\underset{(-)}{\overset{*}{\mathrm{C}}}\mathrm{HMe{\cdot}CH}\underset{(+)}{\overset{*}{=}}\mathrm{CHMe} \longrightarrow \overset{*}{\mathrm{C}}\mathrm{HMeCl{\cdot}CH}\overset{*}{=}\mathrm{CHMe} \longrightarrow \quad \text{(XIII.)}$$

(XI.) (XII.)

$$\mathrm{OH{\cdot}CHMe{\cdot}CH}\overset{*}{=}\underset{(+)}{\mathrm{CHMe}}$$

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[37] *J.*, 1927, 2554.

[38] *J.*, 1926, 1477.

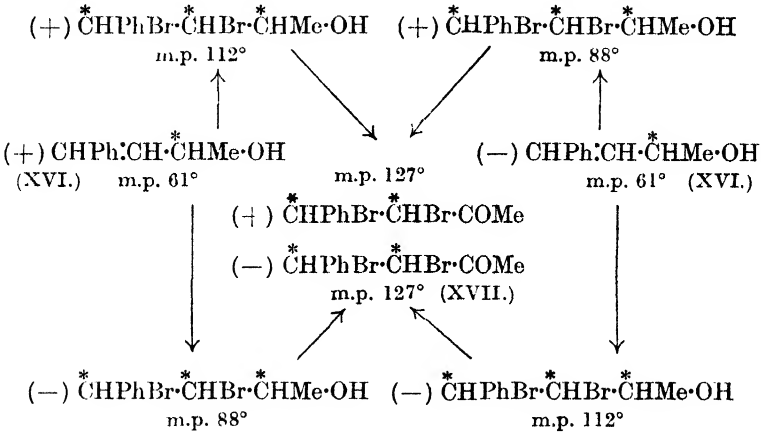
[39] *J. Amer. Chem. Soc.*, 1936, **58**, 1963.

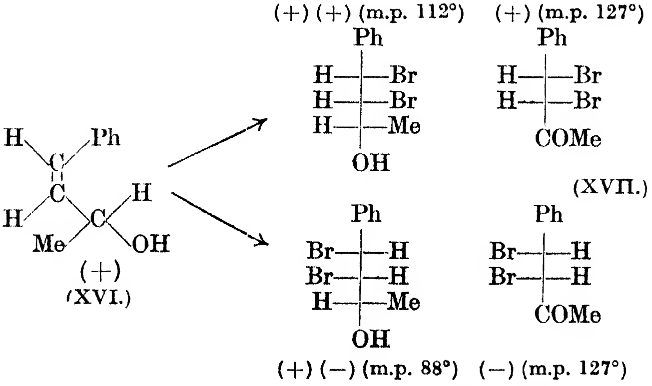
[40] *J.*, 1936, 576.

Yet, whilst catalytic reduction of (XI) gave optically pure (−) methyl-*n*-propylcarbinol, that of (XIII) gave the *dl*-carbinol. Continuation of this work[41] showed that (XI) gave a (+) dibromide (XIV), oxidised to the (+) ketone (XV), whereas (XIII) gave an inactive dibromide, which was oxidised to an inactive ketone :

$$(\mathrm{XI}) \longrightarrow \underset{(\mathrm{XIV.})}{\mathrm{OH{\cdot}\overset{*}{C}HMe{\cdot}\overset{*}{C}HBr{\cdot}\overset{*}{C}HMeBr}} \longrightarrow \underset{(\mathrm{XV.})}{\mathrm{COMe{\cdot}\overset{*}{C}HBr{\cdot}\overset{*}{C}HMeBr}}$$

The authors point out that these results are inconclusive, since (XIII) has not been shown to be *structurally* identical with (XI), but extension of the work to γ-phenyl-α-methylallyl alcohol has led to results of unusual interest. This (+) alcohol (XVI) combines with bromine to give a mixture of two dibromides, which may be (*a*) oxidised to a (−) ketone (XVII) or (*b*) separated by crystallisation into (+) and (−) isomerides :





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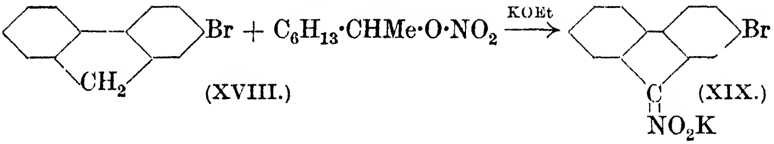
[41] J. Kenyon and S. M. Partridge, *J.*, 1936, 1313.

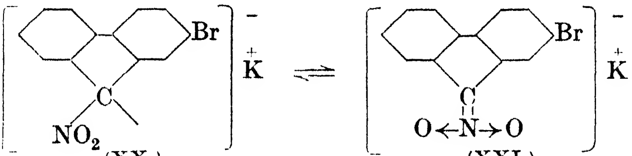
Although this is not an asymmetric synthesis as defined by A. McKenzie,[42] it is a similar type of process, since the original asymmetric centre responsible for " inducing " dissymmetry elsewhere in the molecule is removed, and optical activity is found in the product or products. The new type of process invites elaborate extension, and it is to be hoped the investigators will exploit it fully, and thereby give us more information from which to form views as to the physical basis of the inducing mechanism. In this connexion, reference should be made to a paper by C. K. Ingold and C. L. Wilson, which is dealt with elsewhere.[30]

J. T. Thurston and R. C. Shriner[43] have continued their studies on asymmetric synthesis, and now show that 2-bromofluorene (XVIII) with *d-sec.*-octyl nitrate in presence of potassium ethoxide gives the potassium salt (XIX) of 2-bromo-9-nitrofluorene, which is feebly but definitely dextrorotatory :



(XVIII.) (XIX.)

The activity of the potassium salt is attributed to the presence of some (XX) in equilibrium with the inactive (XXI) :



(XX.) (XXI.)

Restricted Rotation.—An interesting study has been made[44] of the relative rates of racemisation, in boiling glacial acetic acid, of a series of optically active amides (XXII). The results obtained are as follows :

R.	R′.	Period of half racemisation (hours).	Ratio.
H	H	4½	1·2
Me	Me	3¾	1
Et	Et	19½	5·2
H	Me	45	12
H	Et	156	42

The fact that ·CO·NH$_2$ is more effective than ·CO·NMe$_2$ suggests that the tautomeric form ·C(OH):NH may be responsible, and for this reason it would be interesting to know the relative rates of race-

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[42] See, for example, " Ergebnisse der Enzymforschung," 1936, V, 58.

[43] *J. Amer. Chem. Soc.*, 1935, **57**, 2163.

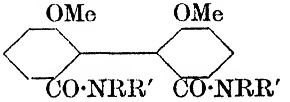
[44] C. Y. Hsing and R. Adams, *ibid.*, 1936, **58**, 587.

misation of the two amides in which R and R′ were, respectively, H and Pr$^{\alpha}$, and H and Pr$^{\beta}$.

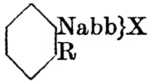
2 : 2′- and 3 : 3′-Dichlorodiphenyl have electric moments of 1·91 D and 1·80 D, respectively. The high moment of the former compound is attributed[45] to London dispersion forces between the chlorine atoms.

The reporter has pointed out[46] that optical activity due to restricted rotation should be demonstrable in suitably di-ortho-substituted benzenes, such as (XXIII), where R is a large atom such as iodine or a group with a large "dynamic effect." Attempts to obtain evidence that such optical activity is possible have been described.[47] The cinchonine salt of *N*-benzenesulphonyl-6-nitro-2 : 4-dimethylaniline showed no mutarotation.

(XXII.)

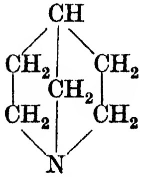


(XXIII.)

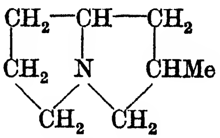


Stereochemistry of Tervalent Nitrogen and Arsenic.—Attempts continue to be made[48] to resolve tervalent nitrogen derivatives, and G. Kamai[49] has endeavoured to resolve certain tervalent arsenic compounds. So far no success has been achieved with either type. In connexion with tervalent nitrogen, it may be noted that two new types of cyclic compounds have been synthesised, the stereochemistry of derivatives of which would be worth investigating. V. Prelog and E. Cerkovnikov[50] have prepared *bicyclo*-[1 : 2 : 2]-azaheptane (XXIV), the lower homologue of that attractive substance, quinuclidine, and G. Menschikov[51] has obtained 2-methylpyrrolizidine (XXV).

(XXIV.)



(XXV.)



L. Pauling,[52] from infra-red absorption results, concludes that pyrrole probably consists of two kinds of molecules, in one of which

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[45] G. C. Hampson and A. Weissberger, *J. Amer. Chem. Soc.*, 1936, **58**, 2111.

[46] Chemical Society Discussion, Jan. 16th, 1936.

[47] H. C. Tuan, T. T. Hsü, and E. I. F. Hsü, *J. Chinese Chem. Soc.*, 1936, **4**, 131.

[48] E. V. Menon and D. H. Peacock, *J. Indian Chem. Soc.*, 1936, **13**, 104; J. Kenner and F. S. Statham, *Ber.*, 1936, **69**, 187.

[49] *Ber.*, 1935, **68**, 1893.

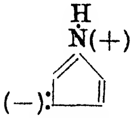
[50] *Annalen*, 1936, **525**, 292.

[51] *Ber.*, 1936, **69**, 1802.

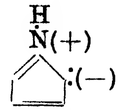
[52] *J. Amer. Chem. Soc.*, 1936, **58**, 94.

the imino-hydrogen is in the plane of the ring, in the other (XXVI) at an angle to it. The first kind can have four variations (XXVII—XXX), and all of these are in resonance with (XXVI):

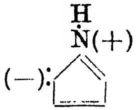
(XXVI.)



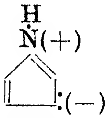
(XXVII.)



(XXVIII.)



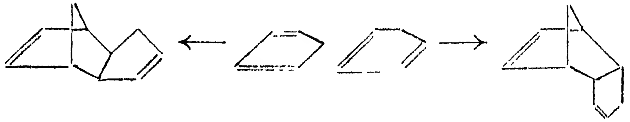
(XXIX.)



(XXX.)

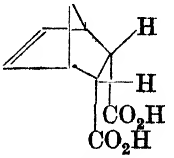
In carbazole and tetraphenylpyrrole the number of "ionic" forms is so much larger that the proportion of non-planar molecules becomes vanishingly small.

"*Steric Course of Addition and Substitution Reactions.*"—A series of very interesting papers have appeared with this title, and under the authorship of K. Alder and G. Stein. In Part I[1] it is pointed out that the polymerisation of *cyclo*pentadiene gives the *endo*-compound (II) at the ordinary temperature and the *exo*-compound (I) at higher temperatures:

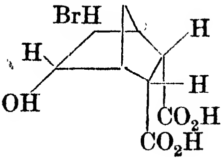


(I.) (II.)

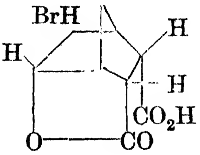
The addition product of maleic anhydride to *cyclo*pentadiene leads only to the *endo*-compound (III). This is proved in the following way: When the product (III) is treated with bromine in aqueous solution, (IV) is formed, and this, in presence of acetyl chloride, gives the lactone (V). The change (IV) ⟶ (III) is effected by means of zinc-copper couple, and therefore a configurative change at this stage is improbable. Further evidence of configuration is that (V) with alcoholic alkali gives the dilactone (VI).



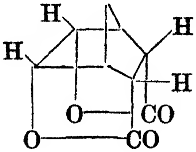
(III.)



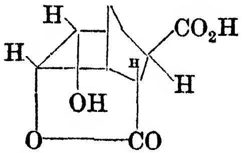
(IV.)



(V.)



(VI.)



(VII.)

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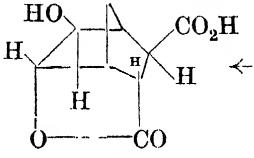
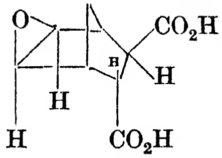
[1] *Annalen*, 1934, **514**, 1.

It may be noted that this dilactone can be distilled unchanged, although it melts at 266°. It is unaffected by hot concentrated nitric acid, but sodium methoxide converts it into the lactone-hydroxy-acid (VII) (*endo* OH; *exo* CO_2H), which is, as would be expected, acetylated, but not lactonised, by boiling acetic anhydride.

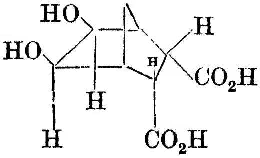
The stereoisomeric lactone-hydroxy-acid (VIII) is obtained from the cyclic ether (IX). The acid (VIII) also is merely acetylated by boiling acetic anhydride. Completely opposed to the dilactone (VI) is the acid (X), obtainable from (III) by Wagner oxidation.



(VIII.)

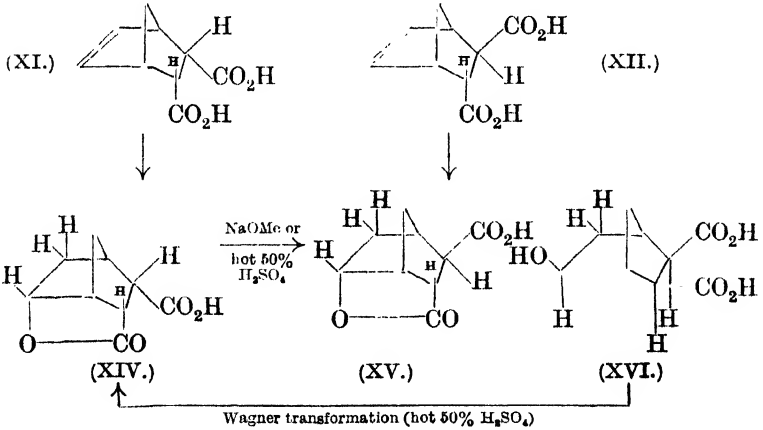


(IX.)

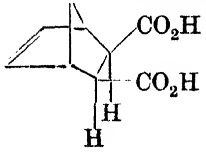


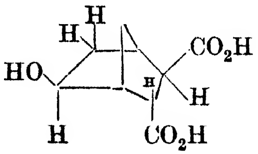
(X.)

Another method of investigating configurations of the *cyclo*-pentadiene–maleic anhydride adduct was treatment with 50% sulphuric acid, which causes addition of the elements of water across the ethylenic linkage. Three acids were taken: (XI≡III), the straightforward adduct (*endo-cis* acid); (XII), its *trans*-isomeride, obtained from it; and (XIII), the *exo-cis*-acid obtained from the dibromide of (XI) by a series of reactions. These three acids, when hydrated, behaved as shown below:



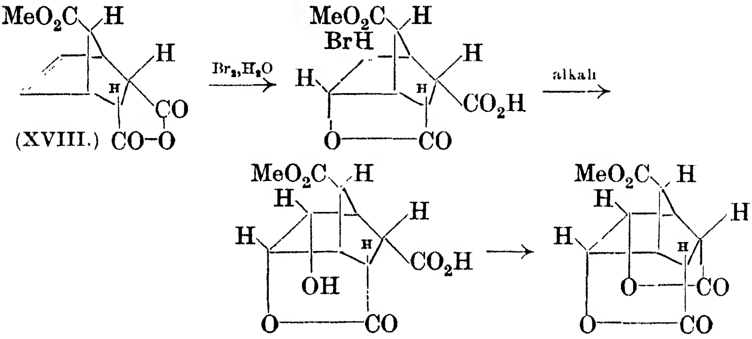
(XIII.)





(XVII.)

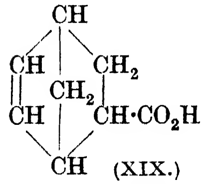
The configuration (XVIII) of the adduct of maleic anhydride to methyl *cyclo*pentadiene-1-carboxylate was established by similar methods:



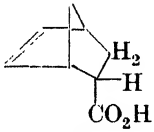
(XVIII.)

so that this addition also occurs sterically in one direction.

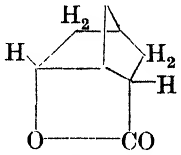
In Part II,[2] the authors discuss the addition of acrylic acid and of acraldehyde to *cyclo*pentadiene, the former giving 2 : 5-*endo*methylene-Δ^3-tetrahydrobenzoic acid (XIX). The adduct in the case of the acid is mainly crystalline, but part is an oil. The crystalline form is proved to be the *endo*-compound (XX), and the oil is probably the *exo*-compound.



(XIX.)



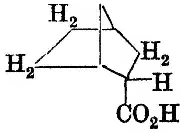
(XX.)

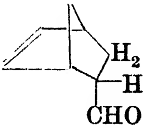


(XXI.)

If the adduct is treated with 50% sulphuric acid, the lactone (XXI) is formed, showing that the carboxyl group was in the *endo*-position. Reduction of (XX) gives (XXII), and since this is also formed by reducing the adduct of acraldehyde and *cyclo*pentadiene, and oxidising the product, this adduct also must possess the *endo*-configuration (XXIII).

(XXII.)





(XXIII.)

The addition of crotonaldehyde and that of *trans*-crotonyl chloride to *cyclo*pentadiene is less easily worked out. It is not certain whether

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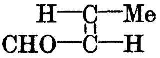
[2] *Annalen*, 1934, **514**, 197.

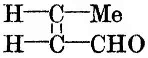
crotonaldehyde obtained by dehydrating aldol is pure *trans-* (XXIV) or contains some *cis*-isomeride (XXV), for F. Kaufler[3] found that oxidation gave mainly crotonic acid, but also appreciable quantities of *iso*crotonic acid. Crotonaldehyde and *cyclo*pentadiene combine to give two adducts, *cis* and *trans*. *trans*-Crotonic acid does not combine with *cyclo*pentadiene, nor does fumaric acid. Fumaryl chloride, on the other hand, combines readily with the diene to give *trans*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalic acid. Similarly, *trans*-crotonyl chloride readily combines with *cyclo*pentadiene, the possible products, after hydrolysis, being (XXVI) or (XXVII). Since the (only) product is converted by 50% sulphuric acid into the lactone (XXVIII), the hydrolysed adduct is (XXVI) and not (XXVII). Again, one of the crotonaldehyde–*cyclo*pentadiene adducts must be (XXIX), since, when it is reduced (ethylenic linkage), and then oxidised, it gives an acid (XXX) which is also formed by reducing *trans*-2 : 5-*endo*methylene-6-methyl(*exo*)tetrahydrobenzoic acid (*endo*) (XXVI).

(XXIV.)

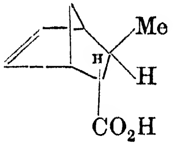


$$\begin{matrix}H-C-Me\\ \Vert\\ CHO-C-H\end{matrix}$$

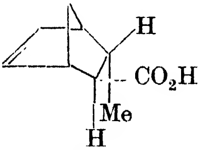
(XXV.)



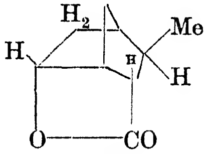
$$\begin{matrix}H-C-Me\\ \Vert\\ H-C-CHO\end{matrix}$$



(XXVI.)

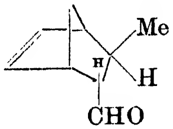


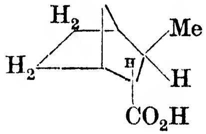
(XXVII.)



(XXVIII.)

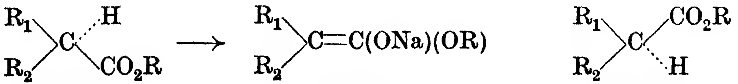
(XXIX.)





(XXX.)

In Part III,[4] the authors apply their methods to the relationship between borneol and *iso*borneol. It is pointed out that, when an ester (XXXI) is treated with sodium methoxide, the sodium enoxide (XXXII) may, on acidification, give (XXXI) or (XXXIII), as a general rule. The *endo-cis*-methyl *bicyclo*heptanecarboxylate (XXXIV), when submitted to this process, gives only the *trans*-form



(XXXI.) (XXXII.) (XXXIII.)

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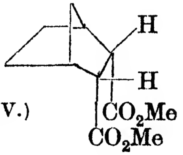
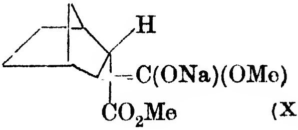
[3] *Monatsh.*, 1929, **53**, 119.

[4] *Annalen*, 1934, **514**, 211.

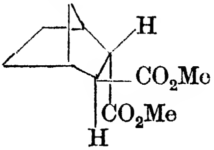
(XXXVI) through the monoenoxide (XXXV), an effect due to the influence of the un-enolised carbomethoxyl group. On the other hand, the enoxide of (XXXVII) is reconverted entirely into (XXXVII).



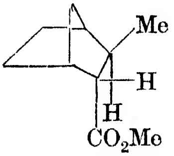
(XXXIV.)



(XXXV.)

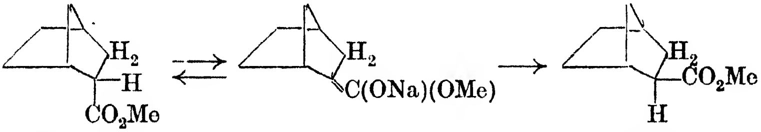


(XXXVI.)



(XXXVII.)

The simplest example of this type is that of (*endo*) 2 : 5-*endo*-methylene-hexahydrobenzoic acid (XXXVIII), the neighbouring carbon atom (CH_2) being symmetrical, so that the only factor which could affect the result of sodium methoxide treatment is the configuration of the *bicyclo*heptane system itself. It is found that the product of this treatment is at least 70—80% *exo* ester (XXXIX).



(XXXVIII.) (XXXIX.)

The *endo*-acid (XXXVIII) has been converted[5] by the Hofmann and Curtius methods into norbornylamine ($CO_2H \longrightarrow NH_2$). The *exo*-acid, similarly treated, gave rise to a second base. It is known that in these degradations configurational changes are unusual, and the two bases, from (XXXVIII) and (XXXIX), are therefore, respectively, (XL) (*endo*) and (XLI) (*exo*). The physical properties of *endo*- and *exo*-types may be determined, and the accumulated data used for determination of configuration in cases where chemical methods cannot be applied.

Komppa and Beckmann treated the *endo*-amine (XL) with nitrous acid, and obtained an alcohol, β-norborneol, of unknown configuration, and different from the α-norborneol obtained by reducing norcamphor (XLII). Both alcohols are oxidised to the latter, and are therefore diastereoisomerides (XLIII; XLIV). It was found by Alder and Stein that the new *exo*norbornylamine (XLI), when treated

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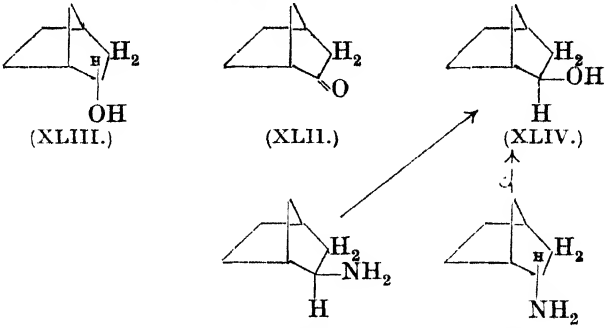
[5] G. Komppa and S. Beckmann, *Annalen*, 1934, **512**, 172.

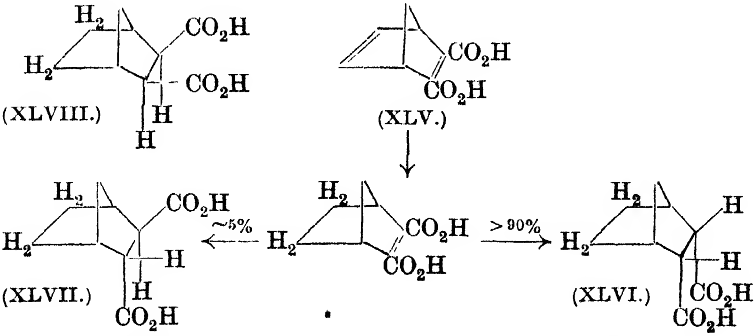
with nitrous acid, gave the same alcohol as the *endo*-amine (XL), one amine therefore undergoing this change with complete inversion of configuration. By analogy with the change of the *endo*-acid (XXXVIII; Me = H) into the *exo*-acid (XXXIX; Me = H), it is assumed that the *endo*-amine (XL) will undergo inversion in passing into the alcohol and that the *exo*-amine (XLI) will not. The alcohol, β-norborneol, produced from both amines, is then the *exo*-compound (XLIV), and α-norborneol is the *endo*-compound (XLIII). This conclusion is supported by other considerations (see also below).


(XLIII.) (XLII.) (XLIV.)

(XLI.) (XL.)

Komppa and Beckmann had already concluded that α-norborneol was configuratively related to *iso*borneol, and β-norborneol to borneol, since the last two substances showed similar resistance to dehydration. In spite of the fact that β-norborneol is dehydrated to norbornylene and borneol to camphene (Wagner rearrangement), Alder and Stein regard the above conclusion as sound, *iso*borneol having the *endo* OH and borneol the *exo* OH arrangement.

Parts IV and V[6] of this series of papers deal with phenylazide reactions, and will not be of general interest, but in Part VI[7] the



(XLVIII.) (XLV.)

(XLVII.) (XLVI.)

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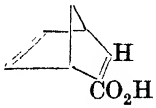
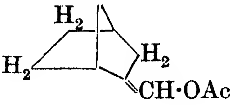
[6] *Annalen*, 1935, **515**, 165, 185.

[7] *Ibid.*, 1936, **525**, 183.

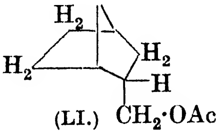
authors return to the study of acids and to borneol and *iso*borneol. It is shown that catalytic reduction, under various conditions, of 3 : 6-*endo*methylene-$\Delta^{1:4}$-dihydrophthalic acid (XLV), or of its methyl ester, gives the *endo-cis*-acid (XLVI; see XXXIV). The *trans*-acid (XLVII) is formed only in traces, and the *exo-cis*-acid (XLVIII) is not formed at all. It therefore follows that addition of hydrogen occurs almost exclusively *cis* and *exo* to the bridge. Similarly, catalytic reduction of 2 : 5-*endo*methylene-$\Delta^{1:3}$-dihydrobenzoic acid (XLIX) gives mainly (XXII).



(XLIX).



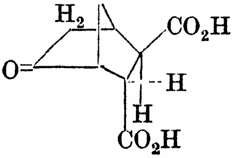
(L.)

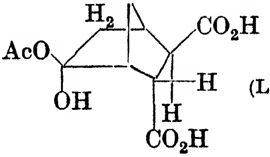


(LI.)

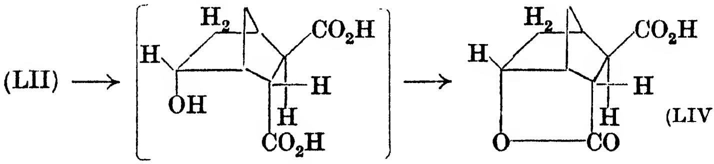
exo-Hydrogenation also occurs with a semi-cyclic ethylenic bond (L ⟶ LI).

Another interesting study is that of the reduction of *trans*-3 : 6-*endo*methylene-4-ketohexahydrophthalic acid (LII), which, when acetylated, gives (LIII), the latter giving (LII) by thermal decomposition. Catalytic reduction, or reduction by means of sodium and alcohol, of (LII) also takes place *exo* to the bridge, the

(LII.)




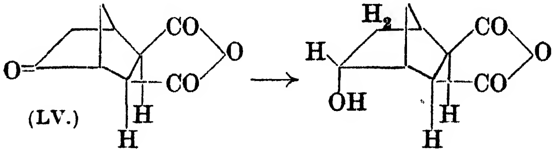
(LIII.)



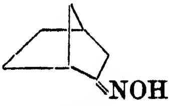
(LIV.)

trans-lactone (LIV) being the chief product. Had *endo*-addition of hydrogen occurred, the hydroxy-acid formed would not have lactonised.

exo-Addition of hydrogen also occurs with *exo-cis*-3 : 6-*endo*-methylene-4-ketohexahydrophthalic anhydride (LV).



(LV.)



(LVI.)

Similarly, norcamphoroxime (LVI) is catalytically reduced *exo*, so that *endo*norbornylamine (XL) is formed. The *exo* mode of addition is therefore characteristic of the *bicyclo*heptane system, and this fact may be made use of for determination of configuration. For example, since norcamphor (XLII) is reduced to α-norborneol, the latter is almost certainly the *endo*-hydroxy-compound (XLIII), and β-norborneol the *exo*-isomeride (XLIV). This confirms the configurations suggested above.

In Part VII[8] the authors show that application of the above methods proves that in *iso*borneol and neobornylamine on the one hand, and in borneol and bornylamine on the other, the hydroxyl and amino-groups are similarly spaced.

E. E. T.

2. CARBOHYDRATES.

Monosaccharides, Disaccharides, and Glycosides.

Some interesting observations have been recorded on the reactions between glucose and bases, marked differences being apparent in the course of the transformations brought about respectively by calcium hydroxide and by sodium hydroxide. In the former case the intermediate product decolorises dichlorophenolindophenol and reacts with iodine in acid solution at a stage when mannose, but no appreciable amount of fructose, can be isolated from the reaction mixture. On the other hand, with sodium hydroxide the unstable intermediate product reacts neither with acid iodine nor with dichlorophenolindophenol, and fructose, but not mannose, can be isolated after the reaction has proceeded at p_H 12 for 24 hours at 30°. The explanation advanced is that with calcium hydroxide the enolic form is produced without rupture of the pyranose ring, whereas the less stable enol formed in the presence of sodium hydroxide has the open-chain structure.[1]

Studies have been made of the synthesis of *d*-fructose and *d*-sorbose from *d*-glyceraldehyde under the influence of *N*/100-barium hydroxide. It appears that the first stage involves the slow transformation of *d*-glyceraldehyde into dihydroxyacetone, followed by a more rapid condensation between the latter and *d*-glyceraldehyde. The product is essentially a mixture, in equal proportion, of *d*-fructose and *d*-sorbose, *d*-psicose and *d*-tagatose being absent. This indicates that there is preferential formation of those products in which the hydroxyl groups attached to the third and the fourth carbon atom have opposite configurations. The configuration

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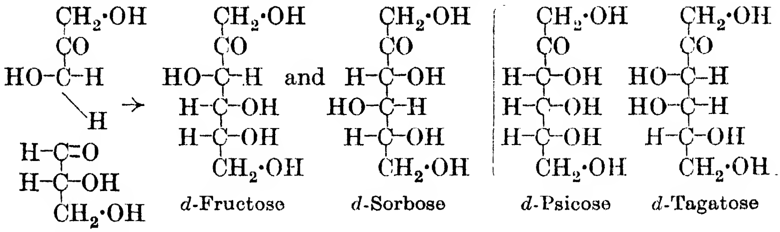
[8] *Annalen*, 1936, **525**, 221.

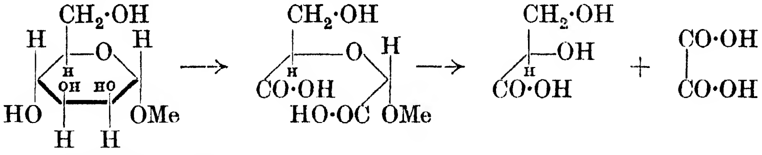
[1] A. Kusin, *Ber.*, 1936, **69**, 1041.

of the *d*-glyceraldehyde is not affected and aldol condensation with dihydroxyacetone must therefore occur immediately, and before formation of any *dl*-glyceraldehyde from the intermediate enolic form. Further evidence on this point is provided by the observation that, if the production of dihydroxyacetone is stopped by using *d*-glyceraldehyde monoacetone in place of *d*-glyceraldehyde, such condensation as takes place involves C_2 of the second reacting molecule and leads to the formation of branched-chain sugars.[2]



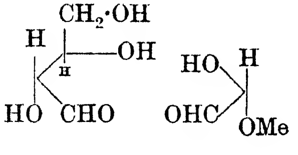
d-Fructose *d*-Sorbose *d*-Psicose *d*-Tagatose

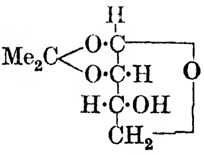
Several papers concerned with the oxidation of sugars and sugar derivatives have been published. One of the most remarkable of these deals with the oxidation of α-methylmannopyranoside and α-methylglucopyranoside by periodic acid and by barium hypobromite. The reaction with periodic acid had been shown previously to involve fission of the molecule at some point other than between C_5 and C_6 [3] and it is now shown [4] that the successive application of periodic acid and bromine water results in the complete elimination of C_3 with fission of the molecule between C_2 and C_3 and between C_3 and C_4. A similar series of changes takes place when barium hypobromite is used. The product (II) from α-methylmannoside (I) after hydrolysis by hot water and oxidation by bromine gives rise to oxalic acid and *d*-glyceric acid. The substance (II) is also obtained



(I; α-methylmannoside.) (II.)

(III.)





(IV.)

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[2] H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, 1936, **19**, 519.

[3] P. Karrer and K. Pfaehler, *ibid.*, 1934, **17**, 766.

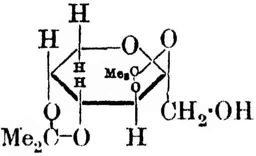
[4] E. L. Jackson and C. S. Hudson, *J. Amer. Chem. Soc.*, 1936, **58**, 378.

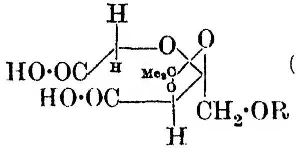
by oxidation of α-methylmannopyranoside or α-methylglucopyranoside by periodic acid, followed by bromine. It will be apparent that the isolation of *d*-glyceric acid in these reactions shows that the oxygen of the ring must be attached to C_5 and further corroborative evidence is thus provided of the presence of the pyranose ring in the stable form of α-methylmannoside and α-methylglucoside.

It is probable that fission between C_2 and C_3 occurs in other oxidative degradations of methyl glycopyranosides. For instance, treatment of α-methylglucopyranoside with lead tetra-acetate gives glyoxal and glycollic acid with only a trace of formaldehyde, the suggested explanation being that the primary products of the reaction are those shown as (III) above.[5] Lead tetra-acetate continues to have useful applications in the sugar group and one of the latest examples is its use in the preparation of *d*-threose, which can be readily isolated as its monoacetone derivative (IV) after oxidation of benzylidene arabitol by lead tetra-acetate.[6] The same reagent can be employed in certain cases to determine whether or not the primary alcoholic group is esterified in sugar phosphoric acids, no formaldehyde being produced if the primary group is united with phosphoric acid.[7]

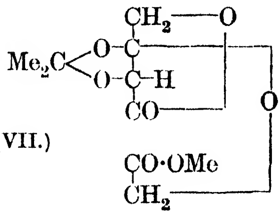
Another example of oxidative degradation may be cited in which fission of the pyranose ring takes place between two of the carbon atoms, leaving the oxygen of the ring untouched. This occurs during the oxidation of β-fructosediacetone (V) to the monoacetone derivative of a dicarboxylic acid, named by the authors

(V.)

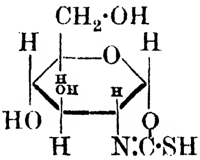




(VI.)



(VII.)



(VIII.)

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[5] P. Karrer and K. Pfaehler, *Helv. Chim. Acta*, 1934, **17**, 363.

[6] M. Steiger and T. Reichstein, *ibid.*, 1936, **19**, 1016.

[7] H. von Euler, P. Karrer, and B. Becker, *ibid.*, p. 1060.

furtondicarboxylic acid. In alkaline solution the oxidation of (V) proceeds normally, the primary alcoholic group being oxidised to carboxyl, but in neutral solution the oxidant attacks preferentially the CH linkings of the etherified hydroxyl groups and then breaks the C–C link between the fourth and the fifth carbon atom. The constitution of the product (*iso*propylidene furtondicarboxylic acid; VI, R = H) has now been proved by a study of its transformation products. For example, the silver salt of (VI, R = H) gives on methylation the lactone (VII), and the latter in turn on treatment with methyl-alcoholic hydrogen chloride gives in 90% yield hydroxytetronic acid. Methylation of (VI, R = H), besides yielding (VII), gives rise also to the fully methylated derivative, methyl γ-methoxy-$\alpha\beta$-*iso*propylidenedioxy-β-carbomethoxy-methoxy-*n*-butyrate (methyl ester of VI, R = Me), which decomposes after hydrolysis with formation of glycollic acid, $CH_2(OH)\cdot CO_2H$, acetone, carbon dioxide, and (probably) dihydroxymethylacetone. It follows therefore that (VI) has the constitution indicated above.[8]

Considerable attention continues to be paid to partly substituted derivatives of the sugars and a few examples of recent results will now be mentioned. The properties of glucose 4-phosphate (obtained from 1 : 2 : 3 : 6-tetra-acetyl β-glucose by phosphorylation and subsequent deacetylation) have been studied and differences between the behaviour of the 3-, 4-, and 6-glucose phosphates have been noted.[9] The 5-methyl ether of glucose has been obtained by the following procedure: glucose diacetone 3-*p*-toluenesulphonate is converted into the corresponding monoacetone derivative, from which by means of benzoyl chloride 6-benzoyl 3-*p*-toluenesulphonyl glucose 1 : 2-monoacetone is obtained. The 5-methyl derivative is then readily formed and after alkaline hydrolysis, followed by acetylation, 5-methyl 3 : 6-diacetyl glucose monoacetone is obtained. The last substance gives in turn 5-methyl glucose monoacetone and removal of the acetone residue leaves 5-methyl glucose. The question of a possible Walden inversion during removal of the *p*-toluenesulphonyl group is considered by the author, and evidence adduced against its occurrence. The final product (5-methyl glucose) displays remarkable properties which require further investigation. It reduces Fehling's solution and permanganate in the cold and appears to exist partly in the aldehyde form, since it gives a colour immediately with Schiff's reagent.[10] With regard to other monomethyl ethers of the hexoses it is now stated that

[8] H. Ohle and N. Senger, *Ber.*, 1936, **69**, 160.

[9] A. L. Raymond, *J. Biol. Chem.*, 1936, **113**, 375.

[10] L. von Vargha, *Ber.*, 1936, **69**, 2098.

Pacsu's supposed 4-methyl galactose [11] is really 6-methyl galactose and that this author's claims concerning the corresponding 4-methyl mannose cannot be substantiated.[12]

A new type of glucose derivative (μ-thiolglucoxazoline) (VIII) has been obtained by treating glucose with potassium thiocyanate in the presence of 12*N*-hydrochloric acid. This does not reduce Fehling's solution, but appears to form a salt with sodium hydroxide. It is readily decomposed by phenylhydrazine with formation of glucosazone. With alkaline hydrogen peroxide the thiol group is removed and replaced by hydroxyl, the resulting substance, μ-hydroxyglucoxazoline, being now capable of reducing Fehling's solution.[13]

The use of acetone derivatives of the sugars as a means of preparing partly substituted sugars is further exemplified by the recent work of H. Ohle and his collaborators, who have made a special study of 5 : 6-anhydroglucose 1 : 2 - monoacetone. The 5 : 6-anhydro-ring can be opened by a variety of reagents and numerous 6-substituted glucoses are thereby obtainable. Amongst these may be mentioned 6-thioglucose monoacetone (obtained by the action of hydrogen sulphide and barium hydroxide on the anhydro-compound), from which 6-thioglucose is obtainable.[14] In addition various sulphides, sulphonic acids and 6-halogenohydrins may be prepared from the anhydro-substance. Furthermore, 6-amino-derivatives (including, *e.g.*, 6-glucosylpiperidine) [15] are produced when amines are used to open the anhydro-ring, and by a similar procedure the 6-phthalimide derivative is obtained.[16]

Interesting and unexpected results have been encountered in a study of the condensation products of *o*-nitrobenzaldehyde with sugars and glycosides. Glucose, mannose, and galactose each give rise to a di-*o*-nitrobenzylidene derivative, one of the benzylidene groups being united through the 4 : 6 positions. These derivatives contain one hydroxyl group, but resist acylation, and are otherwise noteworthy in that under the influence of light they isomerise, giving 4-*o*-nitrosobenzoates in place of 4 : 6-*o*-nitrobenzylidene derivatives. 4 : 6-*o*-Nitrobenzylidene derivatives of methylglycosides are found to behave similarly. That the high reactivity of the *o*-nitro-group is responsible for these transformations is shown by

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[11] E. Pacsu and A. Löb, *Ber.*, 1929, **62**, 3104; E. Pacsu and C. von Karry, *Ber.*, 1929, **62**, 2811.

[12] J. Munro and E. G. V. Percival, *J.*, 1936, 640.

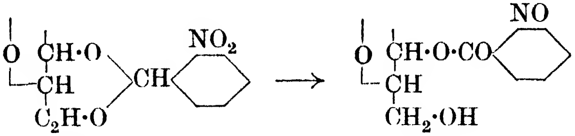
[13] G. Zemplén, A. Gerecs, and M. Rados, *Ber.*, 1936, **69**, 748.

[14] H. Ohle and W. Martens with, in part, M. Andrée and E. Euler, *Ber.*, 1935, **68**, 2176.

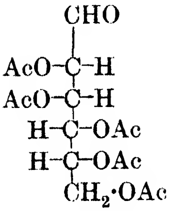
[15] H. Ohle, E. Euler, and W. Malerczyk, *Ber.*, 1936, **69**, 1636.

[16] H. Ohle and E. Euler, *ibid.*, p. 1022.

the fact that the corresponding *m*-nitrobenzylidene derivatives are stable to light. The behaviour of these substances appears to be yet further complicated by the occurrence of Walden inversions during the isomerisation, but full understanding of the mechanism involved is at present incomplete on account of the difficulties experienced in removing the nitrobenzylidene and nitrosobenzoyl residues.[17]

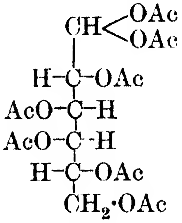


Several papers have been published on the chemistry of the open-chain or aldehydo-forms of sugars. Experiments carried out by M. L. Wolfrom and L. W. Georges show that *d*-mannose displays a pronounced tendency to react in the open-chain form. For example, penta-acetyl aldehydo-*d*-mannoseoxime (obtained by the action of oxalic acid in methyl alcohol on the corresponding hexa-acetate) is converted by the action of nitrous acid into aldehydo-*d*-mannose penta-acetate (IX). The last-named substance reacts with semicarbazide in the usual way, giving a semicarbazone identical with the product obtained by acetylating mannosesemicarbazone with acetic anhydride and pyridine in the cold. The penta-acetate



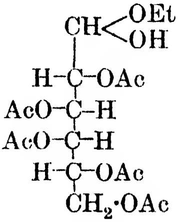
$$\begin{array}{c} CHO \\ AcO-C-H \\ AcO-C-H \\ H-C-OAc \\ H-C-OAc \\ CH_2\cdot OAc \end{array}$$

(IX.)



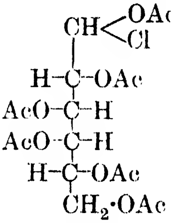
$$\begin{array}{c} CH<^{OAc}_{OAc} \\ H-C-OAc \\ AcO-C-H \\ AcO-C-H \\ H-C-OAc \\ CH_2\cdot OAc \end{array}$$

(X.)



$$\begin{array}{c} CH<^{OEt}_{OH} \\ H-C-OAc \\ AcO-C-H \\ AcO-C-H \\ H-C-OAc \\ CH_2\cdot OAc \end{array}$$

(XI.)



$$\begin{array}{c} CH<^{OAc}_{Cl} \\ H-C-OAc \\ AcO-C-H \\ AcO-C-H \\ H-C-OAc \\ CH_2\cdot OAc \end{array}$$

(XII.)

(IX) reacts with mercaptan in the presence of zinc chloride, giving the corresponding penta-acetyl *d*-mannose diethylmercaptal,[18] which may also be obtained from mannose diethylmercaptal.[19]

In last year's Report (p. 275) reference was made to the isolation of a hepta-acetyl derivative of *dl*-galactose.[20] General methods for the preparation of these hyper-acetylated derivatives have now been described and applied in the preparation of hepta-acetates of

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[17] I. Tanasescu and E. Craciunescu, *Bull. Soc. chim.*, 1936, [v], **3**, 581, 1511, 1517.

[18] M. L. Wolfrom and L. W. Georges, *J. Amer. Chem. Soc.*, 1936, **58**, 1781.

[19] N. W. Pirie, *Biochem. J.*, 1936, **30**, 374.

[20] F. Micheel, H. Ruhkopf, and F. Suckfull, *Ber.*, 1935, **68**, 1523.

d-galactose (X), *d*-glucose, and *d*-mannose and hexa-acetates of *l*-arabinose, *l*-rhamnose and *d*-xylose.[19, 22] These hyper-acetates are much more stable than the free aldehydo-sugars. Somewhat surprisingly, the hepta-acetate of *dl*-galactose has been encountered as an acetolysis product of agar.[21] Since hydrolysed agar on acetylation gives rise only to sugar acetates with a ring structure, these results suggest that in intact agar the *dl*-galactose portion occurs in a form other than that with a furanose or pyranose ring (probably the open-chain form) and that the hepta-acetate is derived from agar by processes in which acetylation has preceded hydrolysis. The results of Micheel,[20] according to which a *d*-galactose derivative is converted into the hepta-acetate of *dl*-galactose, render it to some extent uncertain whether the isolation of *dl*-galactose from agar can by itself be regarded as proof of the pre-existence of both forms of galactose in the complex molecule. In this instance, however, there is independent evidence of the presence of *l*-galactose in the products of hydrolysis of agar.

Another class of open-chain sugar compounds is now available for investigation. These compounds are the open-chain analogues of the cyclic halogeno-sugar acetates, *e.g.*, acetobromoglucose. In the open-chain series the halogeno-derivatives are prepared by the action of the appropriate halogen compound (acetyl bromide, etc.) on the hemi-acetal (XI) of the acetylated aldehydo-sugar. In this way the 1-chloro- (XII), 1-bromo- and 1-iodo-derivatives of hexa-acetyl aldehydogalactose are obtained. The same acetylated halogeno-compounds are produced also by the interaction of acetyl chloride and acetyl bromide on aldehydogalactose penta-acetate.[22]

The tendency of galactose to yield furanose derivatives is demonstrated in a novel way by the formation in good yield of β-ethylgalactofuranoside when the diethyl or the dibenzyl mercaptal of galactose is treated with ethyl alcohol and mercuric chloride at low temperatures in the presence of mercuric oxide.[23]

Observations in the disaccharide series show that maltosesemicarbazone and cellobiosesemicarbazone and their acetyl derivatives possess ring structures and by successive oximation and acetylation of cellobiose hepta-acetate a cellobioseoxime nona-acetate, also containing a ring structure, is formed. If, however, cellobioseoxime is acetylated in the cold, a nona-acetate of the aldehydo-form is obtained. From the latter by partial hydrolysis with oxalic acid in methyl alcohol the corresponding octa-acetate is produced and finally by the action of nitrous acid on the octa-

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[21] N. W. Pirie, *Biochem. J.*, 1936, **30**, 369.

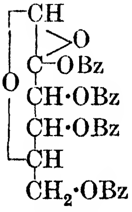
[22] M. L. Wolfrom, *J. Amer. Chem. Soc.*, 1935, **57**, 2498.

[23] E. Pacsu and J. W. Green, *ibid.*, 1936, **58**, 1823.

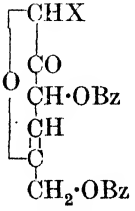
acetate there is obtained the octa-acetate of aldehydocellobiose. In this series of changes it is to be noted that the behaviour of the cellobiose derivatives on acetylation is the reverse of that of the corresponding glucose compounds.[24]

Benzoyl derivatives of aldehydo-sugars have been further investigated. For example, M. L. Wolfrom and C. C. Christman[25] treated arabinose diethylmercaptal with triphenylmethyl chloride and then with benzoyl chloride. To the resulting substance the structure 2 : 3 : 4-tribenzoyl 5-triphenylmethyl *l*-arabinose diethylmercaptal is ascribed. Successive removal of the triphenylmethyl group and the mercaptal residues yields a tribenzoyl *l*-arabinose which probably possesses a pyranose ring structure. The latter is readily benzoylated to the tetrabenzoyl derivative, which is obtainable also by direct benzoylation of arabinose. The above tribenzoyl derivative may be obtained also from the tribenzoyl *l*-arabinosidyl bromide produced by the action of hydrogen bromide in acetic acid on arabinose tetrabenzoate. Whilst the above reactions are considered to support the pyranose structures of the tri- and tetra-benzoates, the possibility of acyl group migration renders the argument somewhat inconclusive. For data concerning numerous benzoates, both open-chain and ring forms, of galactose, mannose and glucose the original paper should be consulted.

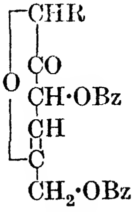
Further investigations of the extraordinary changes undergone by glucosone and its derivatives are reported by K. Maurer and R. Böhme.[26] These experiments are concerned principally with 2 : 3 : 4 : 6-tetrabenzoyl glucosone, the preparation of which from benzobromoglucose *via* tetrabenzoyloxyglucal has been described previously.[27] This substance (XIII), unlike the corresponding acetyl derivative, does not give a hydrate and the ethylene oxide ring opens with extreme difficulty except in the presence of halogen acid. The ensuing change involves the elimination of two molecules of benzoic acid with formation of a non-reducing substance (XIV)



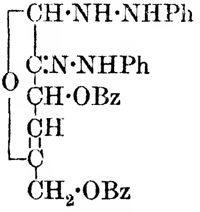
(XIII.)



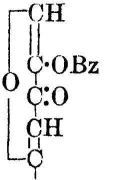
(XIV.)



(XV.)



(XVI.)



(XVII.)

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[24] M. L. Wolfrom and S. Soltzberg, *J. Amer. Chem. Soc.*, 1936, **58**, 1783; M. L. Wolfrom, L. W. Georges, and S. Soltzberg, *ibid.*, 1934, **56**, 1794.

[25] *Ibid.*, 1936, **58**, 39.

[26] *Ber.*, 1936, **69**, 1399.

[27] K. Maurer and W. Pitsch, *Ber.*, 1933, **66**, 995.

containing a double bond. The halogen in (XIV) cannot be replaced by hydroxyl, but reacts readily with many organic substances, being replaced by OMe, OEt, SEt, NHPh, etc. All such substances (XV) lose the residue R on treatment with phenylhydrazine and give the same osazone (XVI). The rotations of the halogen sugars (XIV) are strongly positive and those of the derived substances (XV) strongly negative. These halogen sugars are therefore the first recorded examples of halogeno-osones, comparable with the ordinary aceto-halogeno-sugars in that they give rise to a series of β-glucosonides, which are the analogues of the β-methylglycosides. These halogen derivatives (XIV) and also the glucosonides (XV) are readily convertible into dibenzoylkojic acid (XVII), a reaction which is used as evidence in support of the view that the double bond in (XIV) and (XV) lies between C_4 and C_5.

It has been known for many years that the dilactone of mannosaccharic acid possesses exceptional properties in that it reduces Fehling's solution and yields iodoform when allowed to react with sodium hypoiodite. The cause of this behaviour and the detailed structure of mannosaccharodilactone are still the subjects of investigation and hitherto this substance has been the only one of its kind known to possess such properties. It is of special interest therefore to find that the corresponding dilactone of saccharic acid behaves in precisely the same way.[28] The preparation of saccharodilactone is beset with special difficulties and can be achieved only by making use of highly purified samples of the well-known monolactone of saccharic acid. The latter substance is purified by recrystallisation from ether in a continuous extraction apparatus—a process which requires many weeks. The purified monolactone is then slowly dehydrated over phosphoric oxide. In aqueous solution the dilactone mutarotates rapidly and the solution neutralises sodium hydroxide immediately. For this reason it is suggested that one of the lactone rings is of the δ-variety. This, however, cannot be regarded as definitely certain and, besides the above-mentioned peculiarities, other anomalies such as the requirement of more than two molecules of alkali for complete neutralisation still await explanation. The chemistry of these dilactones offers problems of special importance and their further investigation will be awaited with interest.

Progress is being made in various directions in the study of both natural and synthetic nucleosides. J. M. Gulland and E. R. Holiday[29] have compared the absorption spectra of adenosine (from yeast nucleic acid) and of inosine (obtained by deamination

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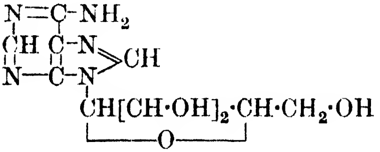
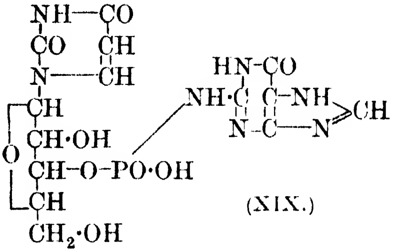
[28] K. Rehorst and H. Scholz, *Ber.*, 1936, **69**, 520.

[29] *J.*, 1936, 765.

of adenosine) with the absorption spectra of methyl derivatives of adenine and hypoxanthine. The absorption shown by adenosine closely resembles that of 9-methyladenine but differs from that of 7-methyladenine, and the absorption spectrum of inosine is similar to that of 9-methylhypoxanthine but different from that of 7-methylhypoxanthine. It is argued therefore that the ribose residues in adenosine and inosine are attached to position 9 of the adenine molecule (XVIII). Furthermore, since muscle adenylic acid gives adenosine under the influence of bone phosphatase and the spectra of adenylic acid and 9-methyladenine are closely similar, it is highly probable that adenylic acid is adenine-9-riboside-5-phosphoric acid. This conclusion differs from the one usually put forward, according to which the ribose residue is regarded as attached to the 7-position. It is of special interest in that a parallel is thereby found between these nucleosides and flavine, in which the ribityl residue is attached to the corresponding nitrogen atom.[30]



(XVIII.)



(XIX.)

Experiments bearing on the mode of union of the four mono-nucleosides in yeast nucleic acid have been instituted. By gentle hydrolysis of yeast nucleic acid guanine-uridylic acid is obtainable. This is monobasic and contains no free amino-group. Union of the guanine and uridylic acid must therefore take place through the phosphate and amino-groups. For these reasons H. Bredereck and G. Richter[31] suggest the formula (XIX) for guanine-uridylic acid.

Investigations of synthetic nucleosides have led to the preparation of substances of the pyranose and furanose series, the latter being of special interest on account of the occurrence of ribofuranose residues in the natural products. Acetobromoglucose and 2 : 4-di-ethoxypyrimidine give a condensation product having the glucose residue in position 1 and this on treatment by alcoholic ammonia

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[30] H. von Euler, P. Karrer, M. Malmberg, K. Schöpp, F. Berg, B. Becker, and P. Frei, *Helv. Chim. Acta*, 1935, **18**, 522; R. Kuhn, K. Reinemund, F. Weygand, and R. Ströbele, *Ber.*, 1935, **68**, 1765.

[31] *Ber.*, 1936, **69**, 1129.

yields 1-*d*-glucopyranosidocytosine.[32] In the furanose series the synthesis of theophylline 5-methyl-*l*-rhamnofuranoside has been achieved by P. A. Levene and J. Compton.[33] This work has involved the preparation and characterisation of both 5-methyl *l*-rhamnofuranose and 4-methyl *l*-rhamnopyranose, concerning which there has previously been some confusion. The α- and β-forms of methyl 5-methyl *l*-rhamnofuranoside are obtained from the two forms of *iso*propylidene *l*-rhamnose and give on hydrolysis the free sugar, which shows no observable mutarotation but is not an aldehydo-sugar. 4-Methyl *l*-rhamnopyranose is available from the mixture of 4- and 5-substituted derivatives obtained when *iso*propylidene rhamnose is methylated by the method of P. A. Levene and I. E. Muskat.[34] The acetobromo-derivatives of 4- and 5-methyl *l*-rhamnose combine with silver theophylline in the usual way and the authors are enabled to compare in detail the behaviour of the theophylline glycosides of 4-methyl *l*-rhamnopyranose and 5-methyl *l*-rhamnofuranose.

Another rhamnoside discussed during the period under review is kaempherol-*l*-rhamnoside (XX), which is now shown to be obtained by enzymic fission of robinine. In addition the hydrolysis gives rise to a new disaccharide, robinobiose, which is *l*-rhamnosido-*d*-galactose. Since robinine can be hydrolysed, giving a trisaccharide (robinose), it is highly probable therefore that the sequence of monoses in robinose is in the order rhamnose, galactose, rhamnose.[35]

In the disaccharide group new syntheses of gentiobiose and of 1-β-glucosidofructose have been reported. The former follows from the interaction of acetobromoglucose with 3 : 5-benzylidene 1 : 2-*iso*propylidene glucose. Catalytic hydrogenation of the resulting mixture left the newly formed disaccharide unchanged but removed the benzylidene group of the starting material, thus permitting ready separation of tetra-acetyl 6-β-glucosido 3 : 5-benzylidene 1 : 2-*iso*propylidene glucose. The acetyl groups were removed by Zemplén's method and thereafter treatment with dilute mineral acid removed the benzylidene and acetone groups and gave rise to gentiobiose. This synthesis in itself proves the presence of a free hydroxyl group at C_6 in the 3 : 5-benzylidene 1 : 2-monoacetone glucose, and other experiments are described in the same paper substantiating the structures assigned to the latter substance and to Levene's 5 : 6-benzylidene 1 : 2-monoacetone glucose.[36] When

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[32] G. E. Hibbert and E. F. Jansen, *J. Amer. Chem. Soc.*, 1936, **58**, 60.

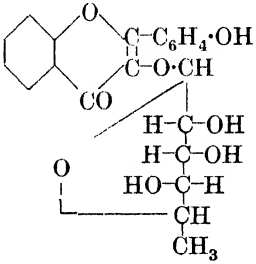
[33] *J. Biol. Chem.*, 1936, **114**, 9.

[34] *Ibid.*, 1934, **105**, 431.

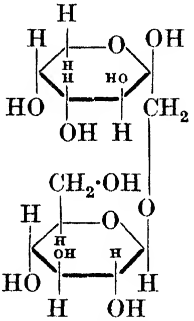
[35] G. Zemplén and A. Gerecs, *Ber.*, 1935, **68**, 2054; cf. C. Charaux, *Bull. Soc. Chim. biol.*, 1926, **8**, 915.

[36] P. Brigl and O. Widmaier, *Ber.*, 1936, **69**, 1219.

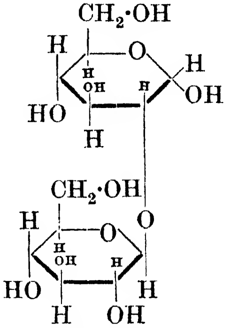
dibenzylidene fructose, the benzaldehyde residues of which are shown to be in the 2 : 3, 4 : 5-positions, is condensed with acetobromoglucose, the tetra-acetyl dibenzylidene derivative of 1-β-glucosidofructose (XXI) is obtained. The acetyl groups are eliminated by alcoholic ammonia, and the benzaldehyde residues by catalytic hydrogenation.[36]



(XX.)



(XXI.)



(XXII.)

K. Freudenberg and K. Soff[37] have studied the action of acetobromoglucose on 4 : 6-benzylidene-α-methylglucoside. Union of the glucose residues takes place through the second carbon atom of the latter substance, giving, after removal of the benzaldehyde, followed by acetylation, 2-β-glucosido-α-methylglucoside hepta-acetate. Transformation of this substance into the free sugar involves the difficult operation of removing the methylglucosidic group without disturbing the glycosidic link between the two glucose residues. This was accomplished by the following method, which should be generally suitable for the isolation of bioses from methylbiosides. The hepta-acetyl methylbioside was allowed to react with acetic anhydride and sulphuric acid under carefully controlled conditions and subsequent treatment with hydrogen bromide in acetic acid gave the acetobromobiose. This with thallium acetate yielded the octa-acetate and the latter in turn was hydrolysed by Zemplén's method to the free sugar. Positions 2 and 3 are available for condensation in the initial reaction with benzylidene methylglucoside, but the observation that the free sugar yields glucosazone at once with phenylhydrazine establishes the structure as 2-β-glucosido-α-glucose (XXII).

Polysaccharides.

Starch and Cellulose.—In a comprehensive paper,[38] Staudinger attempts to elucidate the constitution of starch on the basis of

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[37] *Ber.*, 1936, **69**, 1245; cf. K. Freudenberg and K. Soff, *Ber.*, 1933, **66**, 19.

[38] H. Staudinger and H. Eilers, *Ber.*, 1936, **69**, 819.

a comparison between the viscosities and osmotic pressures of solutions of a series of starch dextrins. On the grounds that in different solvents (formamide, formic acid, water) a starch dextrin shows practically the same specific viscosity; that in any given solvent there is only a small decrease of viscosity with rise of temperature; and that the viscosity of a starch dextrin before acetylation and after deacetylation is the same, Staudinger regards the starch colloidal particle as being a macro-molecule rather than a micelle or aggregate of smaller molecules held by van der Waals forces. If this thesis be accepted, then the particle weight determined by some physical method such as the osmotic pressure method will also be the normal molecular weight and a comparison of the molecular weight so determined with that determined viscosimetrically from the relation $\eta_{sp.}/C_{gm.} = K_m M$ will evaluate the constant K_m. A series of such comparisons carried out on various dextrins (the osmotic pressure figures of W. Biltz[39] were employed) gave for K_m the value of roughly 1×10^{-4}. By analogy with the similar relationship between the cellodextrins and cellulose, it was assumed that this new value of K_m for the starch dextrins would hold also for starch itself. It is concluded from these results that the constant K_m for the starch series is only one tenth of that for the cellulose series and that the cellulose constant (10×10^{-4}) may not be used to evaluate the molecular weight of starch. The new constant for the starch series is derived from somewhat inadequate data, but if it be confirmed and the Staudinger principle of the relationship between molecular-length and viscosity be accepted, the interesting deduction is made that the length of the starch macromolecule is only one-tenth of the length of a cellulose macromolecule of equal molecular weight. Otherwise expressed, starch of molecular weight 50,000 behaves in solution as if it were of the same length as a cellulose of molecular weight 5000. It is suggested, in explanation, that whereas the cellulose molecule consists of a straight chain of glucose units, the molecular chain of glucose units in starch takes a spiral form and that it is the length of this spiral which determines the viscosity of starch solutions. It is pointed out that such a spiral formation would be favoured by the α-glucosidic linkages in the starch molecule. The physical properties of starch compared with those of cellulose and of cellodextrins are also cited as evidence in favour of this view; in particular, the insolubility of starch in Schweitzer's reagent is ascribed to residual valency linkages between the hydroxyl groups in the spiral.

In a recent article[40] W. N. Haworth summarises the position

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[39] *Ber.*, 1913, **46**, 1532.

[40] *Monatsh.*, 1936, **69**, 314.

with regard to present conceptions of the size of polysaccharide molecules. It cannot yet be regarded as established that the starch colloidal particle consists of a single macromolecule of glucose units united by principal valencies as Staudinger postulates. The amount of tetramethyl glucose obtainable on hydrolysis of methylated starch indicates a chain length of some 24—26 units only unless the hypothesis of branching chains is invoked (this has always been envisaged as a possible alternative to the simple straight chain hypothesis) and there does not seem as yet sufficient evidence to justify the conclusion that the colloidal particles may not indeed be aggregates of this simple unit. It is, for instance, well known that derivatives (such as the acetates) which show different degrees of polymerisation according to the method of formation, may be prepared from one and the same dextrin or starch and, moreover, that the original polysaccharide may be regenerated from such derivatives.

Further application of physical methods to the determination of the particle size of the polysaccharides yields results varying over a very wide range. S. R. Carter and B. R. Record [41] have measured the osmotic pressure of acetyl and methyl derivatives of a number of polysaccharides. Two samples of methylated starch from different sources show osmotic pressures corresponding in particle sizes to values of 630 and 140 glucose units, and the surprisingly large values of 3400 and 5400 glucose units are found in the case of methylated glycogen. O. Lamm,[42] using a diffusion method, records a particle weight of 4×10^6 for starch dispersed in zinc chloride solution, and H. B. Oakley and F. G. Young [43] find that methyl glycogen gives osmotic pressures indicating a mean particle weight of 2×10^6 in dilute calcium chloride solution, and of $3{\cdot}4 \times 10^6$ in benzene. Examination of various celluloses by the ultra-centrifuge method has been made by J. K. Chowdhury and T. B. Bardhan.[44] Cotton, jute and bamboo celluloses in Schweitzer's reagent have particle weights representing degrees of polymerisation of 978, 516, and 189 glucose units respectively and the viscoses prepared from these celluloses show particle weights of the same order. A. von Ekenstein [45] uses phosphoric acid in preference to Schweitzer's reagent as a solvent for cellulose, in which solvent the high value of 157,000 (970 glucose units) is found viscosimetrically for the particle weight of Swedish filter

[41] *J. Soc. Chem. Ind.*, 1936, 218.

[42] *Naturwiss.*, 1936, **24**, 508.

[43] *Biochem. J.*, 1936, **30**, 868.

[44] *J. Indian Chem. Soc.*, 1936, **13**, 240.

[45] *Ber.*, 1936, **69**, 549.

paper. Native cellulose is apparently degraded rapidly and at a constant rate in phosphoric acid until the molecular size of a hydrocellulose is attained, after which the rate of degradation is much reduced. It is claimed [46] that intensive grinding of cellulose under water causes degradation of the thread molecules. Thus, after twelve hours, the material shows a mean degree of polymerisation of 300. An attempt is made by W. A. Richardson, R. S. Higginbotham, and F. D. Farrow [47] to determine the particle weights of starches on the basis of their copper numbers and these authors arrive at figures indicating chain lengths varying from 460 to 1470 glucose units.

Little doubt now remains that both starch and cellulose consist of glucopyranose residues united in the first case entirely by α-glucosidic links and in the second by β-glucosidic links. Freudenberg [48] amplifies his observations on the reaction kinetics of starch hydrolysis and confirms his previous conclusions as to the uniformity of the glucosidic linkages. A similar study of the polarimetric curves of the hydrolysis of the Schardinger dextrins reveals the fact that the postulated lævo-glucosan closure in these substances is no longer tenable and the possibility of large closed rings is cautiously suggested. Further studies of this type on cellulose and its oligosaccharides are reported.[49] A monomethyl cellulose (described as hemimethyl cellulose) has been prepared by R. Piwonka [50] by the treatment of ramie cellulose with caustic soda and copper chloride and methylation of the product with methyl sulphate. Hydrolysis yields a monomethyl glucose and evidence is adduced to show that the methyl group is at position 3.

The significance of the phosphoric acid which is associated with certain starches still remains a matter of conjecture. T. Posternak,[51] by the acid hydrolysis of potato-, sago-, or arrowroot-starches, isolated a glucose monophosphate which was shown to be glucose-6-monophosphate, *i.e.*, Robison's ester. By amylolytic hydrolyses of these starches a tetrasaccharide monophosphate was prepared and the latter on further hydrolysis with acid yielded the Robison ester. The author concludes from his studies that, whereas in the starches stored in rhizomes the phosphorus is combined in ester form with the starch, in the cereals the phosphorus is not directly linked to the starch but rather is present in the form of lecithins.

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[46] H. Staudinger and E. Dreher, *Ber.*, 1936, **69**, 1091.

[47] *J. Text. Inst.*, 1936, **27**, T 131.

[48] K. Freudenberg and K. Soff, *Ber.*, 1936, **69**, 1252; K. Freudenberg, G. Blomquist, L. Ewald, and K. Soff, *ibid.*, p. 1258.

[49] K. Freudenberg and G. Blomquist, *ibid.*, 1935, **68**, 2070.

[50] *Ber.*, 1936, **69**, 1965.

[51] *Helv. Chim. Acta*, 1935, **18**, 1351.

Recent investigations of J. Barsha and H. Hibbert[52] on the celluloses from spruce- and maple-pulps support the view that no chemical distinction is to be drawn between wood cellulose and cotton cellulose. The former, dispersed in acetone, is methylated with ease and methyl cellulose containing 44·5% of methoxyl is obtained. The assumption of a " resistant portion " in wood cellulose appears to be unwarranted.

Mannans.—Considerable interest attaches to the function of mannose polysaccharides in plant metabolism and to their relationship with the universally distributed glucose polysaccharides. Mannose and glucose polysaccharides are frequently found together; indeed, in Konjak-mannan[53] the polysaccharide is composed apparently of glucose intramolecularly combined with mannose. Ivory nut, on the other hand, contains in essentials mannans only,[54] and *Tubera Salep* contains a mannan (30%) which is associated with starch (30%) and a dextrin material (13%), possibly a mixture of mannose and glucose dextrins. The natural *Salep*-mannan is extractable with cold water and is proved[55] by methylation and hydrolysis to be composed of mannose units combined through the glucosidic groups in the same way (1 : 4) as the glucose units are united in starch or cellulose. The basal chemical structure of *Salep*-mannan is thus the same as that of the mannans A and B of ivory nut.[54] The yield of tetramethyl mannose from the hydrolysis of methylated *Salep*-mannan indicates a chain length of some 60 mannose units (mol. weight 12,000). The viscosities, however, of the mannans and of their derivatives are low in comparison with those of the starches and, if the smallest value of the K_m constant given by Staudinger for starch be utilised in calculating the particle weight of mannan, a value (5,000—10,000) is obtained which is less than that given by the end-group method. In order that the two methods of determination of the molecular weight should give the same value, the K_m constant for the mannan series would need to be of the order 4×10^{-5}. The *Salep*-mannan is fairly soluble in water, but the ivory nut mannans are insoluble, a state of affairs difficult to reconcile with the low molecular weight. The authors suggest that in the latter some measure of lateral coupling of the polysaccharide chains occurs so that the particle approaches more nearly to the spherical form, with a consequent reduction of the viscosity. Such a structure would, of course, be less soluble than the free macromolecule.

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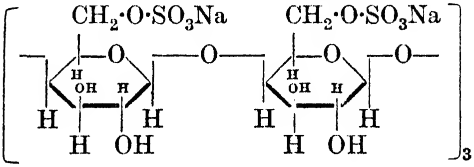
[52] *J. Amer. Chem. Soc.*, 1936, **58**, 1006.

[53] K. Nishida and H. Hashina, *Chem. Zentr.*, 1932, II, 2633.

[54] F. Klages, *Annalen*, 1934, **509**, 159; **512**, 185.

[55] F. Klages and R. Niemann, *ibid.*, 1936, **523**, 224.

Galactans.—A polysaccharide is obtained [56] from a red alga, which apparently is a monosodium sulphate ester of galactan. It gives a diacetyl and a dimethyl derivative, and is hydrolysed by either acid or alkali to galactan. The galactan is methylated to a trimethyl ether and hydrolysis of the latter with hot hydrochloric acid yields a trimethyl galactose. The experiment was not quantitative and no attempt was made to discover any tetramethyl sugar. The trimethyl galactose did not give an osazone and it was oxidised to give arabohydroxydimethoxyglutaric acid. On this basis, the sugar is considered to be 2 : 3 : 6-trimethyl galactose and the following structure is postulated for the original polysaccharide (the glucosidic link is not specified as α or β).



Varianose, prepared by the action of *Penicillium varians* G. Smith, has been investigated by W. N. Haworth, H. Raistrick and M. Stacey.[57] The trimethyl ether of this polysaccharide is hydrolysed by methyl-alcoholic hydrogen chloride to give 2 : 3 : 4 : 6-tetramethyl methylglucopyranoside (14%), 2 : 3 : 6-trimethyl methylgalactopyranoside, and a trimethyl hexoside (14%). The last is considered to be a derivative of either *d*-idose or *l*-altrose. Hence varianose is regarded as a chain of 6 to 8 β-galactopyranose units (1 : 4 glucosidic linkages) with a glucopyranose unit at one end of the chain and a unit of either *l*-altrose or *d*-idose at the reducing end.

Immuno-polysaccharides.—The observation in 1917 by A. R. Dochez and O. T. Avery [58] that the *Pneumococcus* during the early stages of its growth forms a readily soluble substance which diffuses into the culture medium, and the demonstration by M. Heidelberger and O. T. Avery [59] of the polysaccharide nature of this substance (to which the immunological specificity of the organism was ascribed) opened a new chapter in the history of carbohydrate chemistry. In recent years, workers in many fields have given their attention to this aspect of the metabolism of micro-organisms, with the result that it is apparent that the elaboration of specific polysaccharides by micro-organisms is a phenomenon by no means

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[56] W. Z. Hassid, *J. Amer. Chem. Soc.*, 1935, **57**, 2046.

[57] *Biochem. J.*, 1935, **29**, 2668.

[58] *J. Exp. Med.*, 1917, **26**, 477.

[59] *Ibid.*, 1923, **38**, 73.

restricted to *Pneumococcus*. Thus, specific polysaccharides have been demonstrated in Friedlander's bacillus,[60] tubercle bacillus,[61] *Streptococcus viridans*,[62] Shiga's bacillus,[63] *Gonococcus*,[64] *Meningococcus*,[65] *Staphylococcus*,[66] *Cholera vibrio*,[67] typhus bacillus,[68] bacillus aertrycke [69] and anthrax bacillus.[70]

It is not within the province of this Report to discuss the bacteriological aspects of this type specificity and it will simply be pointed out that, although some of these polysaccharides may be capable of conferring active immunity,[69] the majority are at present regarded as haptens in the Landsteiner sense, that is, as substances which do not possess complete antigenic power but are able to precipitate immune-sera prepared against the whole antigen.[63]

The chemical investigation of bacterial polysaccharides is attended by technical difficulties, particularly in their isolation from the culture media, and it is principally in regard to the specific polysaccharides of *Pneumococcus* that sufficient insight has been gained to warrant the present discussion. It seemed at one time that material for such investigation was to be obtained from a purely plant source, namely from gum arabic. A product was obtained [71] by the partial hydrolysis of gum arabic which was comparable in precipitating activity for Types II and III antipneumococcus serum with the bacterial polysaccharides themselves. This was regarded as due to the degraded polysaccharide of gum arabic, particularly as the aldobionic acid obtained by further hydrolysis resembled that obtained by the hydrolysis of the specific polysaccharide of Type III. The aldobionic acid from gum arabic was shown by S. W. Challinor, W. N. Haworth, and E. L. Hirst [72] to be 6-glycuronosido-galactopyranose. More recent work, however, principally by Uhlenhuth,[73] suggests that the immunising activity

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[60] M. Heidelberger, W. F. Goebel, and O. T. Avery, *ibid.*, 1925, **42**, 701.

[61] P. P. Laidlaw and H. W. Dudley, *Brit. J. Exp. Path.*, 1925, **6**, 197; J. H. Mueller, *J. Exp. Med.*, 1926, **43**, 1, 9; E. Chargaff and W. Schaefer, *J. Biol. Chem.*, 1936, **112**, 393.

[62] Lancefield, *J. Exp. Med.*, 1925, **42**, 377.

[63] W. T. J. Morgan, *Biochem. J.*, 1936, **30**, 909.

[64] S. Mutermilch and A. Grunberg, *Compt. rend. Soc. Biol.*, 1935, **120**, 587.

[65] H. W. Scherp and G. Rake, *J. Exp. Med.*, 1935, **61**, 753.

[66] L. A. Julianelle and C. W. Wieghard, *ibid.*, 1935, **62**, 11.

[67] R. W. Linton *et al.*, *Indian J. Med. Res.*, 1935, **22**, 617.

[68] A. Spanedda, *Boll. Soc. ital. Biol. sperim.*, 1936, **11**, 21.

[69] H. Raistrick and W. W. C. Topley, *Brit. J. Exp. Path.*, 1934, **15**, 113.

[70] J. Tomcsik and H. Szongott, *Z. Immunität.*, 1932, **76**, 214.

[71] M. Heidelberger, O. T. Avery, and W. F. Goebel, *J. Exp. Med.*, 1929, **49**, 847.

[72] *J.*, 1931, 258.

[73] P. Uhlenhuth and E. Remy, *Z. Immunität.*, 1934, **82**, 229; 1935, **85**, 328.

may be associated with a nitrogen constituent of gum arabic rather than with the carbohydrate itself, since continued removal of the nitrogen weakens the antigenic effect.

The combined work of Heidelberger, Avery and Goebel on the *Pneumococcus* has made possible a tentative suggestion for the constitutions of the specific polysaccharides of the *Pneumococcus*. An admirable summary is given in a recent paper by M. Heidelberger, F. E. Kendall and H. W. Scherp.[74] The earlier methods of isolation of the polysaccharides involved the use of alkali and it has since been shown that during the process an acetyl group associated with Type I polysaccharide was removed. In the modified method described in the paper cited,[74] the polysaccharides were isolated from culture filtrates without the use of heat, strong acid or alkali. The filtrates were concentrated in a vacuum, repeatedly precipitated with alcohol in the presence of acetic acid and sodium acetate; the proteins removed by denaturation with butyl alcohol and chloroform (following the method of M. G. Sevag [75]), and starch or glycogen by amylolysis. The products were isolated as colourless neutral sodium salts, which yielded solutions of high viscosity. The earlier conception that these polysaccharides were heat-stable needs now to be modified in that heat is shown to bring about a diminution of particle size and also a decrease in the amount of antibody precipitated from homologous rabbit anti-sera.

Type I specific polysaccharide contains nitrogen, acetyl and uronic acid. For a molecular weight of 600 there are present two atoms of nitrogen, one acetyl group and two uronic residues. About half of the nitrogen is free amino-nitrogen, which is acetylated when the polysaccharide is treated with acetic anhydride and sodium carbonate. The original material is amphoteric but, in contrast, the acetylated product titrates sharply with phenolphthalein as indicator and shows an acid equivalent of 319. It would seem that the uronic carboxyl groups are free and that none of the nitrogen is present as acid amide. The earlier suggestion [76] that the uronic acid is galacturonic acid is now confirmed by the isolation of crystalline methyl *d*-galacturonide methyl ester monohydrate formed by the hydrolysis of the polysaccharide with methyl-alcoholic hydrogen chloride. The hypothesis is therefore put forward that the basic unit of the molecule is a trisaccharide containing two molecules of *d*-galacturonic acid and an unidentified substance containing two atoms of nitrogen.

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[74] *J. Exp. Med.*, 1936, **64**, 557.
[75] *Biochem. Z.*, 1934, **273**, 419.
[76] *J. Exp. Med.*, 1925, **42**, 727.

The Type IV polysaccharide resembles that of Type I in that it contains nitrogen, but, whereas the latter contains no acetylated nitrogen, in the former the whole of the amino-nitrogen is acetylated. Further, the Type IV polysaccharide appears not to contain uronic acid.[77] Acid hydrolysis yields an amino-sugar and acetic acid only. In this it bears some relationship to chitin.

Type II and Type III polysaccharides are again different from those of Types I and IV in that their nitrogen content is so small as not to be considered an integral part of the molecule. Investigation has been carried furthest with the polysaccharide of Type III, which yields, on hydrolysis with mineral acid, glucose (9·5%) and an aldobionic acid (85%).[78] The latter is regarded as the basal unit of the polysaccharide in the same sense as maltose is regarded as the basal unit of starch. The aldobionic acid is monobasic, reduces Fehling's solution and on oxidation with alkaline iodine gives a dicarboxylic acid. The latter gives the naphtharesorcinol test, showing the persistence of the uronic residue. It is further hydrolysed by prolonged boiling with acid, and glucose is detected among the products of hydrolysis, the oxidation of which yields saccharic acid but no mucic acid. On this basis it is conjectured that the aldobionic acid is a disaccharide acid formed of glucose and glycuronic acid, the linkage engaging the reducing group of the latter. The methyl ester of the aldobionic acid gives a hepta-acetate (m. p. 249—250°; $[\alpha]_D^{25^\circ} + 40·0^\circ$ in chloroform) which shows no depression of melting point in admixture with a similar derivative from the polysaccharide of pneumococcus Type VIII.[79] The position of the glucosidic bridge on the glucose residue as yet has not been determined. Goebel [80] has synthesised the methyl ester of hepta-acetyl gentiobiuronic acid by the condensation of 1 : 2 : 3 : 4-tetra-acetyl β-glucose with the methyl ester of 1-bromo-triacetyl glycuronic acid. The product, a derivative of 6-glycuronosido-β-glucose, is converted into the α-isomeride by the action of zinc chloride in acetic anhydride. It remains to be seen whether this α-isomeride (m. p. 201—202°; $[\alpha]_D^{23^\circ} + 48·4^\circ$) is identical with the corresponding derivative of the aldobionic acid under discussion. It is of interest to note at this point that Goebel has also synthesised by a similar method the aldobionic acid of gum arabic.[81]

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[77] M. Heidelberger and F. E. Kendall, *J. Exp. Med.*, 1931, **53**, 625.

[78] M. Heidelberger and W. F. Goebel, *J. Biol. Chem.*, 1926, **70**, 613; 1927, **74**, 613.

[79] W. F. Goebel, *ibid.*, 1935, **110**, 391.

[80] R. D. Hotchkiss and W. F. Goebel, *Science*, 1936, **83**, 353.

[81] *Idem, J. Amer. Chem. Soc.*, 1936, **58**, 858.

The nitrogen-free Type II polysaccharide has been much less fully investigated. It has been established that the chief product of its hydrolysis is glucose [68] and it was at first thought that uronic acid was absent. Determinations carried out on the polysaccharide isolated by the method of Heidelberger already described [74] reveal, however, the presence of about 20% of uronic acid.[82]

Reviewing the evidence presented as to the constitution of the *Pneumococcus* polysaccharides, it has to be admitted that no common constituent is discoverable. The specific polysaccharides of Types I, II, III, and VIII contain uronic acid groups, but these are apparently absent from Type IV. Further, the presence of amino-sugars in the molecule is not essential for the development of immunological specificity, since the polysaccharides of Types II, III and presumably VIII contain only traces of nitrogen. The part played by acetyl is peculiar. The acetyl polysaccharide of Type I is actively immunising, whereas the de-acetylated polysaccharide (which was isolated by the alkaline extraction method) is not actively immunising although it precipitates homologous anti-sera.[83]

Mention is made at this point of the blood-group specific carbohydrates, since they have been shown to bear a relationship to the *Pneumococcus* polysaccharides.[84] K. Freudenberg and H. Eichel [85] examined the mixture of specific carbohydrates isolated from the urine of individuals of the blood group A and showed it to contain galactose and *N*-acetylglucosamine. Elimination of the acetyl group results in loss of specificity, which is regained by re-acetylation. A small amount of uronic acid is also present.

Other bacterial polysaccharides which have been investigated chemically include that of *Cholera vibrio* W. 880, which is said to contain arabinose and an aldobionic complex of galactose and glycuronic acid,[86] and that of the *B. dysenteriæ* of Shiga. The latter has been submitted to a careful study by W. T. J. Morgan.[63] The purified specific polysaccharide was rigidly tested for homogeneity; acetylation or benzoylation, followed by its regeneration by treatment with alkali, yielded the specific substance unchanged in all the chemical and immunological properties examined, and fractional precipitation of the polysaccharide from a variety of solvents failed to reveal any heterogeneity. The polysaccharide

[82] M. Heidelberger, W. F. Goebel, and O. T. Avery, *J. Exp. Med.*, 1925, **42**, 727.

[83] W. F. Goebel and O. T. Avery, *ibid.*, 1933, **58**, 731.

[84] E. Witebsky, E. Neter, and H. Sobotka, *ibid.*, 1935, **61**, 703.

[85] *Annalen*, 1935, **518**, 97.

[86] R. W. Linton, D. L. Shrivastava, and B. N. Mitra, *Indian J. Med. Res.*, 1934, **22**, 309.

yields 97% of reducing substances, calculated as glucose, after acid hydrolysis; it has an acid equivalent of 9000 and contains 1·6% of nitrogen and 5% of acetyl. None of the nitrogen is liberated by the prolonged action of nitrous acid, the polysaccharide behaving in this respect more like a derivative of *N*-acetylglucosamine than of free glucosamine. The analytical figures support the view that the whole of the nitrogen is present as an acetylated amino-group. The evidence accumulated suggests that the basal unit of the polysaccharide consists of four hexose molecules and one *N*-acetyl-aminohexose molecule and that this unit is repeated six times in the polysaccharide molecule. Colorimetric tests for *N*-acetylhexosamine indicate that this residue does not constitute the end group of the basal unit.

E. L. H.
S. P.

3. Natural Resins.

General.

The usefulness of the isoprene hypothesis in connection with the structure of abietic acid and other diterpene resin acids has been referred to in these Reports.[1] Later work illustrates the applicability of the hypothesis to the diterpene resinols and continued use has been made of it in attempts to overcome the difficulties presented by the triterpene derivatives.

An examination of the structure of natural products reveals the frequent association of the hexose (C_6) and triose (C_3) units. The application of the C_6—C_3 and C_6—C_3—C_6 units to the chemistry of the alkaloids and plant pigments has been discussed [2] and it is now evident that the C_6—C_3 unit plays an important part in the formation of resin acids and resinols. Propylbenzene derivatives such as safrole and eugenol occur in essential oils, acids such as cinnamic, ferulic and caffeic are common constituents of resins, and coniferyl alcohol is a resinol constituent of gum benzoin. The importance of the C_6—C_3 unit is emphasised by the structural relationships of the more complex phenols which are frequently present in resins. Recent work has shown that many of these phenolic resinols are representatives of a class of compounds, the structures of which may be derived from two C_6—C_3 units, and in all cases of established structure the union is effected at the β-carbon atom of the triose chain. On account of the frequent occurrence of the substances in

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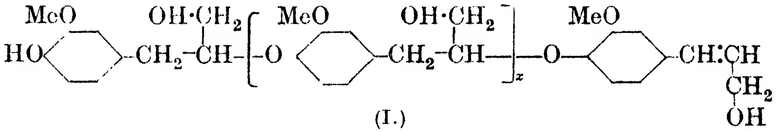
[1] *Ann. Reports*, 1927, **24**, 124; 1932, **29**, 159.

[2] R. Robinson, *Proc. Univ. Durham Phil. Soc.*, 1928, **8**, 1, 15.

wood, the generic term "lignane" is introduced to include all members of this rapidly growing class.[3]

Reference is made to the phytochemical views of Th. Weevers,[4] who points out that substances such as terpenes and resins, which are found in various unrelated families of plants, must have originated from products of metabolism of general occurrence, and the botanical evidence suggests that a modification of the lignin metabolism is responsible for the formation of terpenes, C_6—C_3 derivatives and resins. K. Freudenberg's formula [5] (I) is cited as chemical support for this view. Structure (I), in which several molecules of coniferyl alcohol are polymerised by union of the β-carbon atom of the triose chain with phenolic groups, is unproved, but all theories concerning the structure of lignin,[6] beginning with those of Cross and Bevan in 1893, are expressed in formulæ composed of C_6—C_3 units. Attempts to trace a chemical relationship between (I) and the terpenes are unconvincing.



(I.)

This report deals with the main advances in the chemistry of the diterpene resin acids and resinols since they were last reviewed in 1932; the lignanes are discussed in detail and a summary of recent work on ammoresinol, in which the C_6—C_3 unit is associated with the isoprene unit, forms an appropriate conclusion. A review of triterpene chemistry would be unprofitable at this stage on account of the structural uncertainty in the field.

Diterpenes.

The primary resin acids of the oleo-resins form the subject of several publications. These acids contain labile substances which are converted into abietic acid by the action of heat or acids, and in 1885 Vesterberg isolated *d*- and the labile *l*-pimaric acids from French colophony. In 1924 Ruzicka and Balas proved that *d*- and

[3] A few C_6—C_3 compounds, *e.g.*, tropic acid, contain a branched triose chain; the structure of vulpinic acid—a lichen acid—is derived from the β-union of two such branched C_6—C_3 units.

[4] *Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 183; *Pharm. Weekblad*, 1934, **71**, 62.

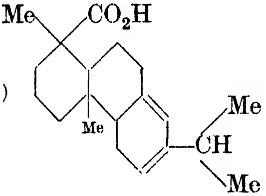
[5] *Annalen*, 1935, **518**, 62. The value of 5—10 is suggested for *x*; compare H. Staudinger and E. Dreher, *Ber.*, 1936, **69**, 1729.

[6] See M. Phillips, *Chem. Reviews*, 1934, **14**, 103; Tschirch and Stock, "Die Harze" (1935), Band II, 527.

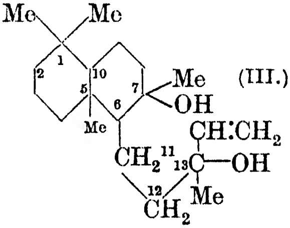
l-pimaric acids were structural isomers, related to the pimanthrene and retene hydrocarbons respectively, and the substitution of the name sapietic acid for *l*-pimaric is now advocated.[7] A third isomeric primary resin acid, proabietic acid, has been isolated from French and American turpentine.[8] Spectroscopic data indicate that the two double bonds of sapietic and proabietic acids are conjugated, and the facile conversion of the acids into abietic acid establishes the carbon framework. Examination of the α_D–time curves suggests that proabietic acid is an intermediate product in the conversion of sapietic into abietic acid.

The position of the double bonds in abietic acid is still uncertain. L. Ruzicka and collaborators [9] prepared a maleic anhydride addition product of abietic acid and suggested (II) as the most probable arrangement. Recently [10] it has been shown that abietic acid and maleic anhydride do not react appreciably below 130°, but the same addition product is readily obtained at room temperature by the action of maleic anhydride with the primary acids of Scots pine (*Pinus silvestris*). The primary acids also react additively with benzoquinone which does not combine with abietic acid, and the conjugation of double bonds demanded by structure (II) is inconsistent with spectroscopic and refractivity measurements made on abietic acid and its ethyl ester.

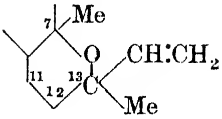
(II.)



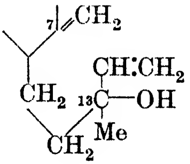
(III.)



(IV.)



(V.)



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[7] T. Hasselstrom and M. T. Bogert, *J. Amer. Chem. Soc.*, 1935, **57**, 2118.

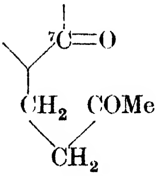
[8] F. Vocke, *Annalen*, 1933, **508**, 11; K. Kraft, *ibid.*, 1935, **520**, 133; 1936, **524**, 1.

[9] L. Ruzicka, P. J. Ankersmit, and B. Frank, *Helv. Chim. Acta*, 1932, **15**, 1289; L. Ruzicka, H. Waldmann, P. T. Meier, and H. Hösli, *ibid.*, 1933, **16**, 169.

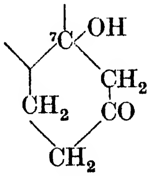
[10] H. Wienhaus, H. Ritter, and W. Sandermann, *Ber.*, 1936, **69**, 2198, 2202.

The constitution of the monoethylenic tertiary diol, sclareol (III),[11] has been confirmed during an investigation [12] of the dicyclic resinols of the New Zealand pines. The monoethylenic manoyl oxide (IV) and the diethylenic tertiary alcohol, manool (V), have been isolated from the silver and pink pines (*Dacrydium colensoi* and *D. biforme*) respectively. The formation of 1 : 2 : 5-trimethylnaphthalene and 1 : 2 : 8-trimethylphenanthrene by dehydrogenating manoyl oxide with selenium suggests that the carbon framework of (IV) is identical with that of agathic dicarboxylic acid and sclareol (III). The oxide ring of (IV) is readily ruptured and cold ethereal hydrogen chloride converts (III), (IV), and (V) into the same trihydrochloride. Manoyl oxide and manool therefore represent cyclic ether and olefinic dehydration products respectively of sclareol. When tetrahydromanool is dehydrated, a mixture of two inseparable, isomeric, dicyclic hydrocarbons is obtained, which on ozonolysis gives a ketone, $C_{18}H_{32}O_4$, and an acid, $C_{16}H_{28}O_2$, and consequently the hydroxyl group of manool is attached to C_{13}. Ozonisation of manool eliminates the methylene and vinyl groups and an oily ketone (VI) is obtained, which is readily isomerised to the keto-alcohol (VII). With excess of methylmagnesium iodide, the keto-alcohol gives a product which is converted into 1 : 7-dimethylphenanthrene by selenium treatment. It follows that C_7 is attached to a methylene group in manool, to one of the tertiary hydroxyl groups in sclareol, and to the oxide ring in manoyl oxide. These three substances therefore represent the diterpene analogues of α-terpineol, terpin hydrate and cineole.

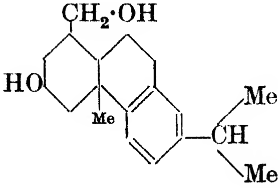
The resin of the silver pine also contains 3-ketomanoyl oxide, which is converted into (IV) by the Wolff–Kishner process. The position of the carbonyl group is determined by condensation with methylmagnesium iodide and dehydrogenation of the product with selenium; 1 : 2 : 5 : 7-tetramethylnaphthalene and an unidentified hydrocarbon, probably 1 : 2 : 6 : 8-tetramethylphenanthrene, were isolated.



(VI.)



(VII.)



(VIII.)

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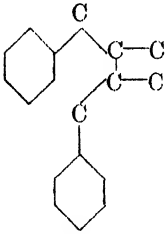
[11] *Ann. Reports*, 1932, **29**, 163; M. Janot, *Ann. Chim.*, 1932, [x], **17**, 5.

[12] J. R. Hosking and C. W. Brandt, *Ber.*, 1934, **67**, 1173; 1935, **68**, 37, 286, 1311; 1936, **69**, 780.

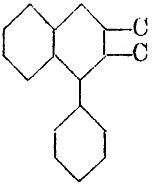
During investigations[13] on the resin of the Japanese cypress (see p. 273) a diol, hinokiol, has been isolated. The proposed structure (VIII), $C_{19}H_{28}O_2$, is uncertain, but the relationship of hinokiol to the diterpenes is inferred from the nature of the dehydrogenation products, which include retene, hydroxyretene (by elimination of the nuclear hydroxyl group), and a phenol, dihydroxyretene.

Lignanes.

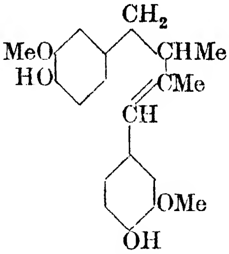
Many lignanes have been isolated from the wood or exuded resin (Überwallungsharz) of the *Coniferæ*, but their occurrence is not confined to this family and representatives have been obtained from the wood, rhizomes, roots, seeds, oils and exuded resins of other unrelated plant families. The lignanes are characterised by the carbon framework (IX) which, in some cases, is modified to the 1-phenylnaphthalene form (X). Hydroxy-, methoxy-, and methylenedioxy-groups are present in the aromatic nucleii and considerable variation occurs in the central portion of the molecule. In the case of guaiaretic acid, the aliphatic chain is composed of carbon and hydrogen only, but this portion of the molecule is usually associated with two or three oxygen atoms of alcoholic, aldehydic, ethereal or carboxylic function.



(IX.)



(X.)



(XI.)

Guaiaretic Acid.—This phenol is the principal constituent of guaiacum resin, obtained from the heartwood of *Guaiacum officinale*. Formula (XI), representing a dimeride of *iso*eugenol, was suggested in 1918;[14] the carbon skeleton of this structure has been proved by the synthesis of *dl*-dihydroguaiaretic acid dimethyl ether,[15] and a synthesis of the diethyl ether[16] establishes the position of the phenolic groups.

Matairesinol, Arctigenin, and Hinokinin.—These substances constitute a closely related group of lactones. The heartwood of matai

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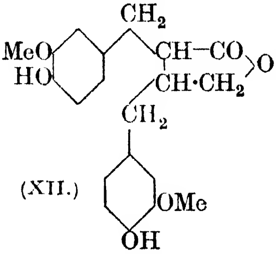
[13] Y. Yoshiki and T. Ishiguro, *J. Pharm. Soc. Japan*, 1933, **53**, 11; S. Keimatsu and T. Ishiguro, *ibid.*, 1935, **55**, 45.

[14] G. Schroeter, L. Lichtenstadt, and D. Irineu, *Ber.*, 1918, **51**, 1587.

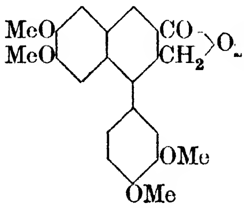
[15] R. D. Haworth, C. R. Mavin, and G. Sheldrick, *J.*, 1934, 1423.

[16] R. D. Haworth and T. Richardson, *J.*, 1935, 120.

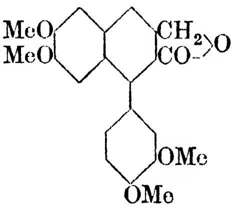
(*Podocarpus spicatus*) is rich in *l*-matairesinol, which was isolated and characterised by T. H. Easterfield and J. Bee,[17] who suggested the molecular formula $C_{19}H_{20}O_6$. This has been modified to $C_{20}H_{22}O_6$ by later work[18] and constitution (XII) has been established. The presence of two vanillyl groups is proved by the isolation of 60% yields of 3-methoxy-4-ethoxybenzoic acid by oxidising the diethyl ether with permanganate. When matairesinol dimethyl ether is treated with lead tetra-acetate, it undergoes cyclo-dehydrogenation and yields two isomeric lactones (XIII) and (XIV) in which the carbon framework of the resinol is preserved. Identification of the lactones with synthetic products obtained by the methods (A) [19] and (B) [20] outlined below leads to formula (XII).



(XII.)

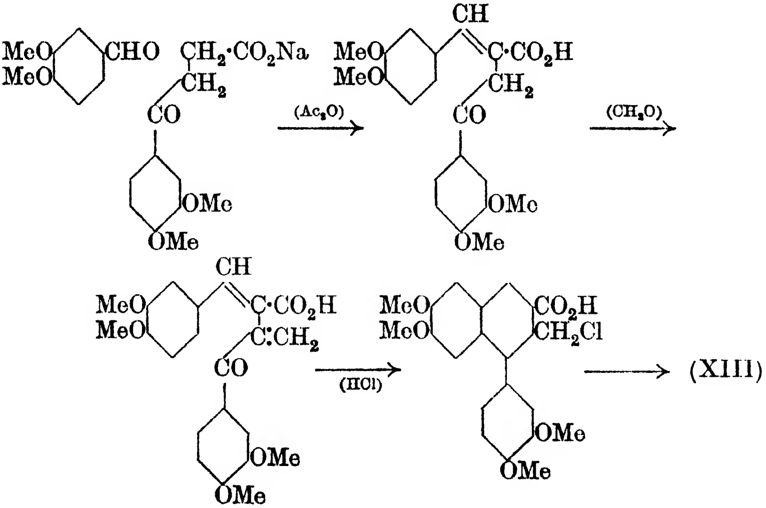


(XIII.)



(XIV.)

Method (A).



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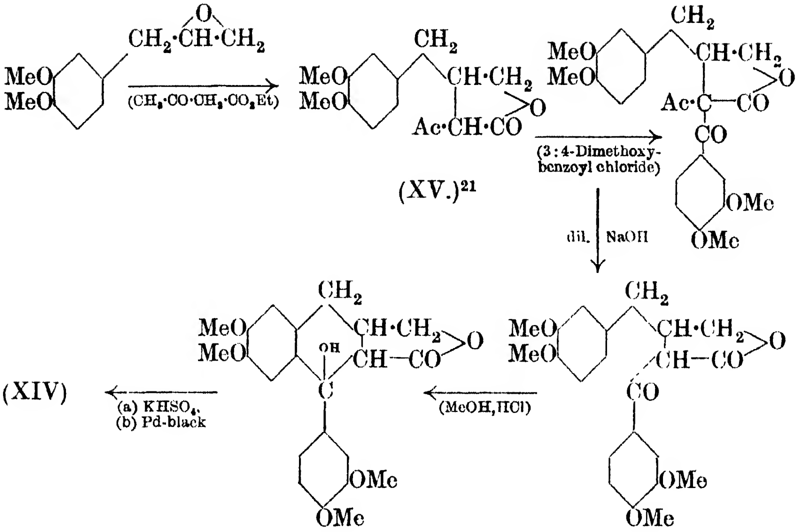
[17] *J.*, 1910, **95**, 1028.

[18] R. D. Haworth and T. Richardson, *J.*, 1935, 633; L. H. Briggs, D. A. Peak, and J. L. D. Woolloxall, *J. Proc. Roy. Soc. N.S.W.*, 1935, **69**, 61.

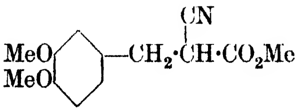
[19] R. D. Haworth, T. Richardson, and G. Sheldrick, *J.*, 1935, 1576.

[20] R. D. Haworth, T. Richardson, and W. Kelly, *J.*, 1936, 725.

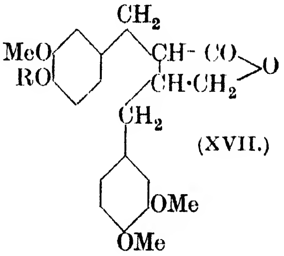
Method (B).



By condensing *O*-methyleugenol oxide with methyl 3 : 4-dimethoxybenzyl-α-cyanoacetate (XVI) and hydrolysing the product, *dl*-matairesinol dimethyl ether has been prepared (method C).[20] The absorption spectra of *dl*- and *l*-matairesinol dimethyl ether are identical, but the synthetic lactone does not yield the lactones (XIII) and (XIV) with lead tetra-acetate. Structure (XII) allows for two inactive resolvable forms [45] and it is suggested that stereochemical differences are responsible for the discrepancy.



(XVI.)



(XVII.)

l-Arctigenin, $C_{21}H_{24}O_6$, which occurs as a glucoside in the seeds of the burdock (*Arctium lappa*) contains a phenolic and three meth-

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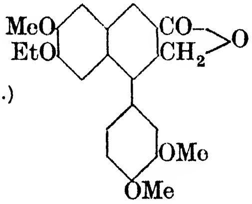
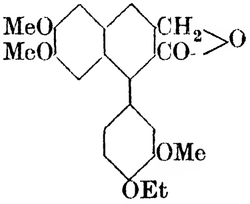
[21] See R. D. Haworth and G. Sheldrick, *J.*, 1935, 636. This earlier synthesis establishes the 1-phenylnaphthalene structure of (XIV), and for this and other reasons, structure (XV) is preferred to an alternative obtained by condensation of the acetoacetate with the ω-carbon atom of the oxide.

oxyl groups. As methylation gives *l*-matairesinol dimethyl ether,[22] arctigenin must be a monomethyl ether of matairesinol, and con-

(XVIII.)



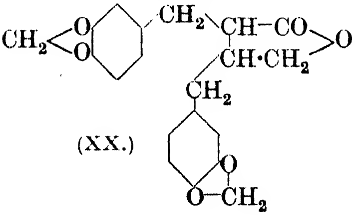


(XIX.)

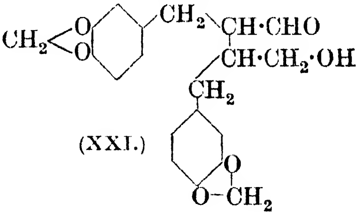
clusive proof of constitution (XVII; R = H) has been obtained.[23] The absorption spectra of the *dl*-lactone (XVII; R = Et), synthesised by method C, and *l*-arctigenin ethyl ether are identical. *cyclo*Dehydrogenation of *l*-arctigenin ethyl ether gives (XVIII) and (XIX), which have been identified with synthetic lactones prepared by methods A and B.

l-Hinokinin, isolated by Y. Yoshiki and T. Ishiguro [13] from the resin of the Japanese cypress (*Cupressus obtusa* [24]), is the optical antipode of *d*-cubebinolide (see p. 274) [13, 25] and the methylenedioxy-analogue of matairesinol. Constitution (XX) is proved by the conversion of *l*-hinokinin into *l*-matairesinol dimethyl ether by alkaline hydrolysis of the methylenedioxy-groups and subsequent methylation.[26]

Synthetic *dl*-hinokinin has been prepared in two ways.[20, 27]



(XX.)



(XXI.)

Cubebin.—This aldehydic lignane, occurring in the unripe fruit of *Piper cubeba*, was studied by E. Mameli,[28] who established the mole-

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[22] J. Shinoda and M. Kawagoe, *J. Pharm. Soc. Japan*, 1929, **49**, 94, 183; T. Omaki, *ibid.*, 1935, **55**, 9.

[23] R. D. Haworth and W. Kelly, *J.*, 1936, 998.

[24] The recommendations of W. Dallimore (Report of the Conifer Conference, 1931) concerning nomenclature of conifers are adopted in this Report.

[25] L. H. Briggs, *J. Amer. Chem. Soc.*, 1935, **57**, 1383; E. Mameli, *Gazzetta*, 1935, **65**, 877, 886.

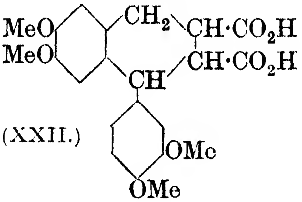
[26] S. Keimatsu and T. Ishiguro, *J. Pharm. Soc. Japan*, 1936, **56**, 19, 61.

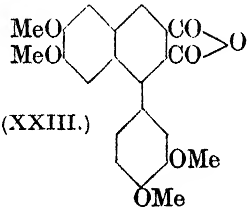
[27] *Idem, ibid.*, 1935, **55**, 185.

[28] *Gazzetta*, 1907, **37**, 483; 1909, **39**, 477, 494; 1912, **42**, 546, 551; 1921, **51**, 353.

cular formula $C_{20}H_{20}O_6$ and showed that cubebin was converted into *d*-cubebinolide by a variety of mild oxidising agents. The identification of cubebinolide with hinokinin indicates the carbon framework of cubebin, but the nature of the aliphatic oxygen atoms has been the subject of controversy. Mameli suggested the presence of two alcoholic groups, but Zerewitinoff determinations reveal the presence of one hydroxyl group only. The isolation of a semicarbazone and methyl *cyclo*acetal prove the presence of a carbonyl group, and structure (XXI) recently suggested [29] is in harmony with the properties of cubebin.

Conidendrin.—The name conidendrin, suggested by H. Erdtman,[30] is adopted for the substance previously known as " sulphite-liquors lactone " and tsugaresinol. It was isolated in 1892 by J. B. Lindsay and B. Tollens [31] from waste liquors, and in 1934 H. Emde and H. Schartner [32] proved that tsugaresinol, obtained by J. Kawamura [33] from the wood of Japanese hemlock (*Tsuga sieboldii*), was identical with the Lindsay–Tollens lactone and also with a lactone isolated from the wood of European spruce (*Picea abies*). The lactone has also been obtained from Matai resin.[19, 34]


(XXII.)


(XXIII.)

The molecular formula and the function of the six oxygen atoms were established by the earlier researches of B. Holmberg,[35] who prepared two important acids by oxidation of conidendrin dimethyl ether. H. Erdtman [36] identified these acids as 2-veratroylveratric acid and (XXII); constitution (XXII), in which the carbon skeleton of conidendrin is preserved, was proved by dehydrogenating the dimethyl ester with lead tetra-acetate to the anhydride (XXIII),

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[29] T. Ishiguro, *J. Pharm. Soc. Japan*, 1936, **56**, 68; R. D. Haworth and W. Kelly, *Chem. and Ind.*, 1936, **55**, 902. Attention may be drawn to the resemblance between the *cyclo*acetal form of (XXI) and the leucoanthocyanidin structure.

[30] *Annalen*, 1935, **516**, 162.

[31] *Ibid.*, 1892, **267**, 353.

[32] *Naturwiss.*, 1934, **22**, 743; *Helv. Chim. Acta*, 1935, **18**, 344.

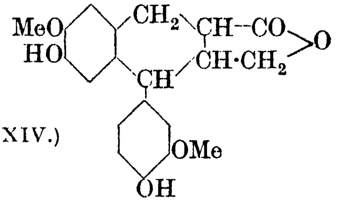
[33] *Bull. Imp. Forestry Exp. Stat. Tokyo*, 1932, **31**, 73.

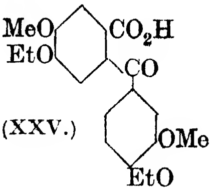
[34] L. H. Briggs and D. A. Peak, *J.*, 1936, 858.

[35] *Svensk Kem. Tidskr.*, 1920, **32**, 56; *Ber.*, 1921, **54**, 2389, 2406; *Ann. Acad. Scient. Fennicae*, 1927, *A*, 29, Nr. 6.

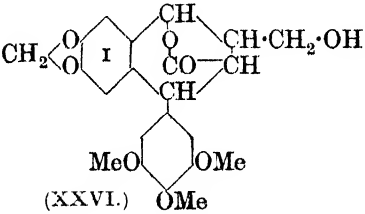
[36] *Annalen*, 1934, **513**, 229.

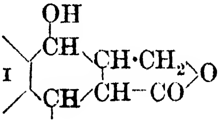
which was compared with a synthetic specimen.[21] Rigid proof of (XXIV) for conidendrin has been obtained. The position of the phenolic groups is established by oxidation of conidendrin diethyl ether to acid (XXV) and the arrangement of the lactonic group is proved by dehydrogenating the dimethyl ether to lactone (XIII) (p. 271).[21]

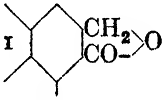

(XXIV.)


(XXV.)

Podophyllotoxin.—The work of Borsche, Späth, and Robertson on podophyllotoxin (XXVI), the crystalline lactone obtained from the resin of Indian and American podophyllin, was reviewed in these Reports for 1932 (p. 191). During the course of their experiments, Späth and his collaborators dehydrated and dehydrogenated picropodophyllin (XXVII) to the lactone (XXVIII). The identity of this lactone with a synthetic product, obtained by method B,[37] provides rigid proof of the carbon framework and the position of the carboxyl and primary alcoholic groups, and indirect proof of the position of the secondary alcoholic group in podophyllotoxin.


(XXVI.)


(XXVII.)


(XXVIII.)

Olivil and isoOlivil.—The dialcoholic cyclic ether structure (XXIX) has been advanced for *l*-olivil,[38] which occurs in the resin of the olive (*Olea europea*). The phenolic groups may be mono- or di-alkylated and the identity of the methyl-ethyl and ethyl-methyl ethers indicates the presence of an axis of symmetry in the molecule. An oxygen atom must be attached to the carbon atom adjoining the aromatic nucleii in order to account for the formation of veratroylformic acid together with veratric acid by the oxidation of olivil dimethyl ether.[39] *l*-Olivil is isomerised to *d*-*iso*olivil (XXX) by the

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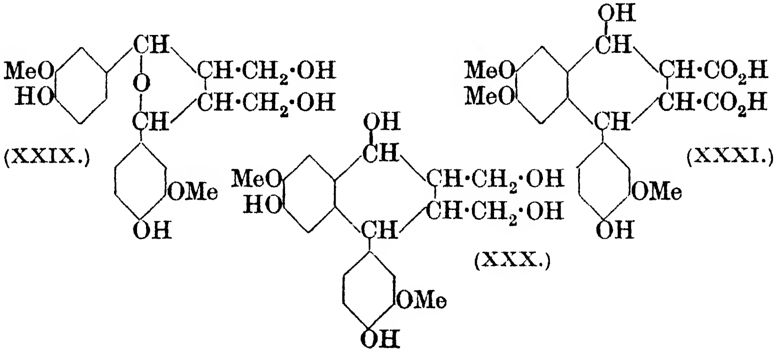
[37] R. D. Haworth and T. Richardson, *J.*, **1936**, **348**.

[38] B. L. Vanzetti and P. Dreyfuss, *Gazzetta*, 1934, **64**, 381.

[39] B. L. Vanzetti, *ibid.*, 1929, **59**, 373; *Monatsh.*, 1929, **59**, 163.

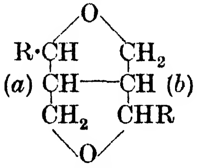
action of formic acid,[39] and as permanganate oxidation of *iso*olivil dimethyl ether yields 2-veratroylveratric acid, the corresponding phthalide[38, 39] and a dibasic acid, $C_{22}H_{24}O_9$,[40] probably (XXXI),


(XXIX.) (XXX.) (XXXI.)

the phenylnaphthalene structure and the presence of two primary alcoholic groups in *iso*olivil are inferred. The position of the phenolic groups has been established by oxidising *iso*olivil diethyl ether to the keto-acid (XXV),[38] and the isolation of lactone (XIV)[41] from chromic acid oxidation of the dimethyl ether is consistent with structure (XXX) for *iso*olivil.

Eudesmin, Pinoresinol, Sesamin, and Asarinin.—The aliphatic portion of these closely related substances contains two ethereal oxygen atoms, probably in the form of a dicyclic ether.

l-Eudesmin[42] was isolated in 1895 by J. H. Maiden and H. G. Smith from the kinos of the cineole-pinene oil bearing species of *Eucalyptus*, *e.g.*, *E. hemiphloia*. It was characterised by R. Robinson and H. G. Smith,[43] who showed that it contained four methoxyl groups and gave 70% yields of 4 : 5-dinitroveratrole with boiling concentrated nitric acid. Eudesmin therefore contains two veratryl groups, and an oxygen atom must be attached to the carbon atoms adjoining the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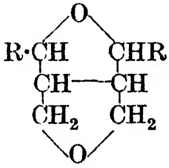
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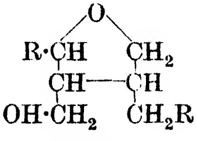
(XXXIV.)

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[40] B. L. Vanzetti, *Rend. Fac. Sci. Univ. Cagliari*, 1934, **4**, 15.

[41] P. Dreyfuss, *Gazzetta*, 1936, **66**, 98.

[42] The nomenclature of members of the lignane class is, in many cases, unfortunate; eudesmin and the sesquiterpene, eudesmene, are chemically unrelated.

[43] *J. Proc. Roy. Soc. N.S.W.*, 1915, **48**, 449.

aromatic nucleii. Several alternative structures including (XXXII) and (XXXIII) (R = 3 : 4-dimethoxyphenyl) were advanced.

H. Erdtman [30, 44] demonstrated that *d*-pinoresinol, isolated by M. Bamberger in 1894 from the Überwallungsharz of the pine (*Pinus nigra*) and spruce (*Picea abies*), yields a dimethyl ether which is the optical antipode of *l*-eudesmin. Proof that pinoresinol contains two vanillyl groups has been obtained in two ways.[45] Nitration of pinoresinol diethyl ether in cold acetic acid gives a mixture of dinitropinoresinol diethyl ether and 4-nitroguaiacol ethyl ether and the yield of the latter is 60% when allowance is made for the diethyl ether undergoing substitution. Secondly, the methylation–ethylation procedure, discussed in connection with olivil, establishes the equivalence of the two phenolic groups in pinoresinol. Assuming the β-linkage of the triose chains, structure (XXXII) or the anhydro-olivil formula (XXXIII) (R = 4-hydroxy-3-methoxyphenyl) is possible for pinoresinol, the former being preferred because pinoresinol has not been converted into a phenylnaphthalene as in the case of olivil.

H. Erdtman [45] has pointed out that the presence of an axis of symmetry limits the configurations of pinoresinol to two *d*- and two *l*-forms of (XXXII) or (XXXIII). Although diastereoisomerism has not been realised with pinoresinol, it is probably displayed in the case of the methylenedioxy-analogues. *d*-Sesamin,[46] which occurs in sesame oil, contains two methylenedioxy-groups, resembles eudesmin in its behaviour with nitric acid, and is therefore formulated as (XXXII) or (XXXIII) (R = 3 : 4-methylenedioxyphenyl). Recently an isomer, *l*-asarinin, showing similar chemical properties has been isolated from *Asarum sieboldii*.[47] By heating *l*-asarinin

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[44] *Svensk Kem. Tidskr.*, 1934, **46**, 229.

[45] *Ibid.*, 1936, **48**, 230, 236. It may be noted that the optically active forms of (XXXIII) require the *trans*-fusion of two five-membered rings, but the active forms of (XXXII) arise from the strainless *cis*-fusion of the rings. This may be used as a further argument in favour of (XXXII), and the failure to dehydrate olivil (XXIX) to (XXXII) may be due to the instability of the optically active forms of this dicyclic system. The reduction of cubebin (XXII) to an optically active diol (Ishiguro [29]) proves, in the absence of optical inversion, that matairesinol, hinokinin, and arctigenin are *trans*-forms. The synthetic *dl*-lactones mentioned on pp. 272, 273 are probably the *cis*-isomers. An extension of the stereochemical relationships suggests that olivil and lignanes of the 1-phenylnaphthalene type are *trans*-forms, and pinoresinol and lariciresinol *cis*-forms. The terms *cis* and *trans* refer to the atoms corresponding to those marked (*a*) and (*b*) in (XXXII).

[46] S. H. Bertram, J. P. K. van der Steur, and H. I. Waterman, *Biochem. Z.*, 1928, **197**, 1; J. Böeseken and W. D. Cohen, *ibid.*, 1928, **201**, 454; J. Böeseken, W. D. Cohen, and C. J. Kip, *Rec. trav. chim.*, 1936, **55**, 815.

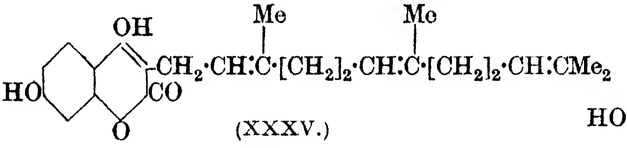
[47] T. Kaku, N. Kutani, and J. Takahashi, *J. Pharm. Soc. Japan*, 1936, **56**, 80.

with alcoholic hydrogen chloride, it is partly converted into *l*-sesamin, and in a similar manner *d*-sesamin is converted into *d*-asarinin. It is concluded that sesamin and asarinin are diastereoisomeric forms of (XXXII) or (XXXIII), but structural isomerism, *e.g.*, (XXXII) and (XXXIII), has not been rigidly excluded.

Unpublished work of the reporter and W. Kelly suggests that lariciresinol, obtained in 1897 by M. Bamberger from the Überwallungsharz of the larch (*Larix decidua*), is represented by structure (XXXIV; R = 4-hydroxy-3-methoxyphenyl).

Ammoresinol.—Structure (XXXV), in which the C_6–C_3 unit is combined with a sesquiterpene chain, has been advanced for the resinol obtained from *Dorema ammoniacum*. Ammoresinol therefore exhibits an interesting relationship with osthol and ostruthin (see these Reports 1934, 257) in which the C_6–C_3 unit is associated with the C_5 and the C_{10} unit respectively.

K. Kunz, H. Weidle, and K. Fischer [48] established the molecular formula and demonstrated the presence of three ethylenic linkages and two hydroxyl groups. The existence of the resorcinol nucleus is proved by the frequent isolation of β-resorcylic acid and resacetophenone derivatives from pyrogenic and oxidation reactions.[48, 49, 50, 51] When ammoresinol is heated in a vacuum, it yields resacetophenone and the coumarin (XXXVI), which was identified with a product synthesised from the chloride of diacetyl β-resorcylic acid and ethyl sodiomethylmalonate.[49] The resorcinol is therefore present in a coumarin ring. Ozonolysis of diacetylammoresinol leads to the aldehyde (XXXVII),[51] identified by conversion into the corresponding acid, which gave β-2 : 4-dihydroxy-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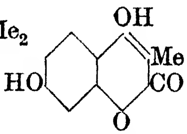
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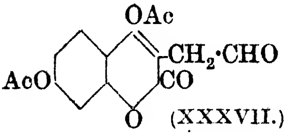
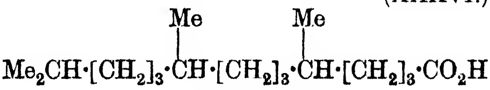

(XXXVII.)



$$Me_2CH\cdot[CH_2]_3\cdot\overset{\mathrm{Me}}{\mathrm{C}}H\cdot[CH_2]_3\cdot\overset{\mathrm{Me}}{\mathrm{C}}H\cdot[CH_2]_3\cdot CO_2H$$

(XXXVIII.)

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[48] *J. pr. Chem.*, 1934, **141**, 350.

[49] E. Spath, A. F. J. Simon, and J. Lintner, *Ber.*, 1936, **69**, 1656.

[50] H. Raudnitz, F. Petru, E. Diamant, K. Neurad, and K. Lannar, *ibid.*, p. 1956. These authors consider further proof is required of the positions of the double bonds; see E. Spath and E. Zajic, *ibid.*, p. 2448.

[51] K. Kunz and L. Hoops, *ibid.*, p. 2175.

benzoylpropionic acid on ketonic hydrolysis. The formation of (XXXVI) and (XXXVII) indicates the point of attachment of the side chain, the nature of which is disclosed by further oxidation experiments. In addition to (XXXVII), ozonolysis of diacetylammoresinol yields acetone,[50] lævulaldehyde [51] and 2-methyl-Δ^2-hepten-6-one,[49] by scission at the double bonds in (XXXV). Oxidation of diacetyl hexahydroammoresinol with permanganate in acetone gives hexahydro-ψ-ionone,[50] whilst with aqueous permanganate, the acid (XXXVIII) was obtained [49] and identified by means of its *p*-xenylamide with an acid, previously obtained from phytol by R. Willstätter, O. Schuppli, and E. W. Mayer.[52]

R. D. H.

4. Aromatic Compounds.

It is some years since a section of the Annual Reports was devoted to aromatic compounds, but the writer is able to deal with only a few aspects of the subject in the limited space at his disposal. In particular he has been unable to include an account of the many mainly theoretical papers dealing with aromatic character and theories of substitution, since these are not suited for brief report.

Benzene.

Structure of Benzene.—A comprehensive investigation of the fine structure of benzene has been undertaken by C. K. Ingold and his co-workers,[1-9] using the methods of long-wave spectroscopy, combined with the possibility of changing the atomic masses and hence the vibration frequencies within the molecule by replacing the nuclear hydrogen atoms by deuterium. By assuming some molecular model, numerical relationships between the frequencies of corresponding normal vibrations in the two isotopically related molecules can be calculated, and then compared with the observed frequency shifts. Since the frequency changes depend on the model assumed, that model which always gives the correct relations is

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[52] *Annalen*, 1919, **418**, 144.

[1] W. R. Angus, C. R. Bailey, C. K. Ingold, and C. L. Wilson, *J.*, 1936, 912.

[2] C. K. Ingold, C. G. Raisin, and C. L. Wilson (appendix by C. R. Bailey and B. Topley), *ibid.*, p. 915.

[3] W. R. Angus, C. K. Ingold, and H. A. Leckie, *ibid.*, p. 925.

[4] C. R. Bailey, J. B. Hale, C. K. Ingold, and J. W. Thompson, *ibid.*, p. 931.

[5] C. K. Ingold and C. L. Wilson, *ibid.*, p. 941.

[6] *Idem, ibid.*, p. 955.

[7] W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, H. A. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, *ibid.*, p. 966.

[8] *Idem, ibid.*, p. 971.

[9] C. L. Wilson, *ibid.*, p. 1210.

proved to be correct. The work has, so far, only been applied to benzene and hexadeuterobenzene; the latter has been obtained in a high degree of purity by an exchange reaction which is discussed later in this section of the Report.

For both benzene and hexadeuterobenzene the authors have investigated in detail the Raman spectra in the liquid state,[3] the infra-red absorption spectra in the vapour and the liquid state,[4] the fluorescence spectra,[5] and the resonance emission spectra.[6] Certain frequencies had been previously reported to occur both in the Raman and in the infra-red spectra, which, according to selection rules, could not be the case if the benzene molecule were a plane regular hexagon possessing a centre of symmetry. These suggested coincident frequencies are discussed [7] in the light of the new experimental results, and no evidence can be obtained for the absence of a centre of symmetry in benzene. In a final discussion of the assignment of vibration frequencies of benzene and hexadeuterobenzene,[8] the authors conclude that all the evidence supports the plane, regular hexagonal model which explains all the salient features of the spectra. The Kekulé structure is incapable of explaining the facts, and there is no evidence indicative of a trigonally puckered molecule.

Heats of Hydrogenation.—Important work on the accurate measurement of the heats of hydrogenation of unsaturated compounds has been carried out by G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan.[10-13] Of particular interest to the present section of the Report are the results recorded for the dienes and benzene, and especially the values of the heats of hydrogenation of the first double bond in these systems, which is given by the difference between the value for the ethylene and that of the corresponding diene, and in the case of benzene by the difference in the values for benzene and 1 : 3-*cyclo*hexadiene. The following figures for the heats of hydrogenation of the first double bond are recorded in gram-calories per molecule :

Allene + H_2	− 41,165	1 : 3-*cyclo*Hexadiene + H_2	− 26,700
1 : 3-Butadiene + H_2 ...	− 26,720	*cyclo*Pentadiene + H_2 ...	− 22,200
1 : 4-Pentadiene + H_2 ...	− 30,660	Benzene + H_2	+ 5,570
1 : 5-Hexadiene + H_2 ...	− 30,400		

The values for 1 : 4-pentadiene and 1 : 5-hexadiene are identical, showing that there is no interaction between the double bonds, the

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[10] *J. Amer. Chem. Soc.*, 1936, **58**, 146.

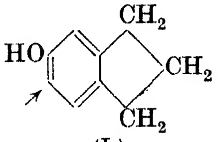
[11] G. B. Kistiakowsky, H. Romeyn, J. H. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, 1935, **57**, 65.

[12] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, p. 876.

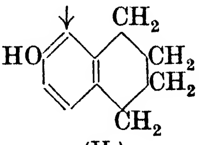
[13] *Idem, ibid.*, 1936, **58**, 135.

values being, in fact, almost identical with that for a compound such as propylene. The strongly exothermic reaction with allene is not unexpected owing to the strained state of the molecule, but the values for both 1 : 3-butadiene and 1 : 3-*cyclo*hexadiene show the mutual stabilisation of the conjugated double bond system, an effect which is still more pronounced in the case of *cyclo*pentadiene. The most striking result is the fact that the hydrogenation of the first double bond of benzene is an endothermic reaction to the extent of 5570 calories, a result which shows the great " resonance " energy of benzene. These resonance energies are calculated as 1800 calories for 1 : 3-*cyclo*hexadiene, 3400 for 1 : 3-butadiene, 6400 for *cyclo*pentadiene, and 36,000 for benzene. It is obvious that these results afford a valuable method for measuring the extent of the interaction of double bonds and the relative degrees of aromatic character of cyclic systems. Further work will be awaited with interest, especially in the case of compounds such as hydrindene (discussed below) where the resonance energy may be expected to be less than in the case of benzene owing to the fixation of the double bonds.

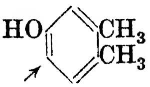
Benzene Derivatives containing Fixed Links.—Hydrindene derivatives. Considerable interest was aroused in 1930 by a paper by W. H. Mills and I. G. Nixon [14] in which it was shown that hydrindene would be in a less strained condition when a single bond was common to the two rings as shown in (I), and that in tetralin the preferred Kekulé configuration would probably be that with a double bond common to the two rings (II).



(I.)



(II.)



(III.)

Experimental support for these conclusions was that diazo-coupling and bromination of the hydroxy-derivatives (I) and (II) took place solely at the positions indicated by the arrows, *i.e.*, only at those carbon atoms which were considered to be doubly bound to the carbon atoms bearing the activating hydroxyl groups. It was, however, pointed out by Mills and Nixon that *o*-4-xylenol (III) is attacked chiefly in position 5, which could mean that the chemical influence alone of the hydrindene ring might be sufficient to explain the observed reactions in the case of the hydroxy-hydrindene (I), and hence the only real evidence for the postulated

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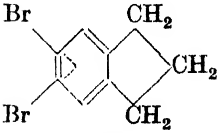
[14] *J.*, 1930, 2510; *Ann. Reports*, 1930, **27**, 131.

effect was the different behaviour of 6-hydroxytetralin (II). Further difficulties in the way of accepting the results as proof of the original hypothesis were, first, that the argument in the case of the tetralin derivative rested upon a number of assumptions difficult of direct proof, and, secondly, because of doubts as to the validity of arguments based on the formation in preponderating amount of one product in a chemical reaction in cases where two isomers might be expected.[15]

Evidence has now been forthcoming from two separate sources to show that in the case of hydrindene the " Mills–Nixon effect " is a real one, but that there is no such effect in the case of tetralin derivatives. The first of these is the work of N. V. Sidgwick and H. D. Springall on the dipole moments of bromohydrindenes and bromotetralins.[16] Their argument is briefly that, if the bonds are fixed in hydrindene, then in 5 : 6-dibromohydrindene (IV) the angle between the two C–Br valencies should be appreciably greater than that in *o*-dibromobenzene and the resulting dipole moment of the group Br–C–C–Br should be measurably smaller in the former case. The observed dipole moment of 5 : 6-dibromohydrindene (IV) was found to be in very close agreement with the moment calculated on the assumption of a fixed double bond between carbon atoms 5 and 6. The moments of the system Br–C–C–Br in the compounds *o*-dibromobenzene, 4 : 5-dibromo-*o*-xylene and 6 : 7-dibromotetralin were found to have the values 2·12 D, 2·13 D, and 2·11 D, whilst the value in the case of 5 : 6-dibromohydrindene (IV) was only 1·78 D. These results clearly indicate a fixation of the links in a hydrindene derivative in a resting state of the molecule (as distinct from a possibly activated form detected by chemical reaction), but free resonance of the aromatic system in tetralin and *o*-xylene.



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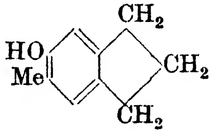

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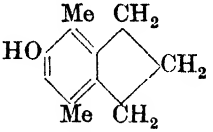

(VI.)

The second evidence is of a chemical nature, but is a much more severe test of the Mills–Nixon hypothesis than the original chemical evidence. L. F. Fieser and W. C. Lothrop[17] prepared the two hydrindene derivatives (V) and (VI) in which one of the two ortho-positions with respect to the hydroxyl group in each case is blocked

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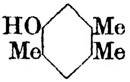
[15] L. E. Sutton and L. Pauling, *Trans. Faraday Soc.*, 1935, **31**, 939.

[16] *Chem. and Ind.*, 1936, **55**, 476; *J.*, 1936, 1532.

[17] *J. Amer. Chem. Soc.*, 1936, **58**, 2050.

by a methyl group. If fixation of the links is permanent, then (V) should be incapable of coupling with diazo-compounds, while (VI) should couple normally. This was actually found to be the case, and the refusal of (V) to give azo-derivatives is particularly striking when compared with the behaviour of ψ-cumenol (VII), which couples with diazo-compounds in the usual manner.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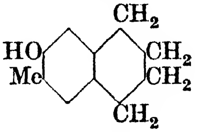
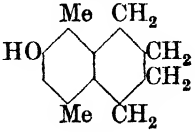
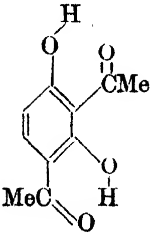

(VIII.)

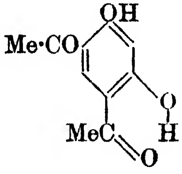

(IX.)

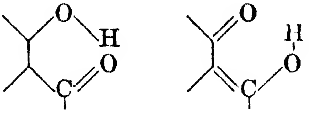
The two tetralin derivatives (VIII) and (IX) both coupled readily with diazotised amines, and thus gave no indication of the Mills–Nixon effect in the tetralin series.

Finally it has been suggested that the stability and ease of formation of certain *o*-quinones derived from hydrindene are due to the fixation of the links in the aromatic nucleus in the position required by the *o*-quinonoid structure.[18, 18a]

Chelate Compounds.—The view that certain simple benzene derivatives might possess fixed double bonds owing to chelation was advanced by W. Baker in 1934.[18] The two isomeric 2 : 4- and 4 : 6-diacetylresorcinols (I and II respectively) differ widely in their physical properties, the former exhibiting the characteristics (volatility, solubility in hydrocarbon solvents, small depression of the melting point under water, mordant dyeing properties, etc.) of a chelate compound such as *o*-hydroxyacetophenone, and the latter closely resembling a non-chelate compound such as *p*-hydroxyacetophenone. The differences between the two isomers was ascribed to the necessity for the *o*-hydroxy and carbonyl groups to be united to mutually unsaturated carbon atoms


(I.)


(II.)


(a.) (b.)

(III.)

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[18] W. Baker, *J.*, 1934, 1680.

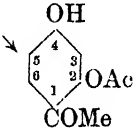
[18a] C. H. Fisher, R. W. Furlong, and M. Grant, *J. Amer. Chem. Soc.*, 1936, 58, 820.

before chelation could occur, a conclusion which is upheld by a comparison of the physical properties of certain pairs of aliphatic compounds, *e.g.*, the enolic form of acetylacetone, $CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3$, and 2-hydroxy-4-ketopentane,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

Owing to this requirement double chelation can occur in (I), but not in (II), which must contain a free hydroxyl group. The necessity for the double bond was originally ascribed to the electromeric effects of OH and CO, but is now regarded as due to the nature of the hydrogen bond, the resonance hybrid derived from the two extreme forms (III*a* and *b*) requiring the fixation of the remaining two double bonds in the benzene ring.[19]

A method was devised for detecting the fixation of double bonds in *o*-hydroxyacetophenones based on the fact that a 4-substituted resorcinol almost invariably undergoes further substitution in the symmetrical position 6, and not in the alternative position 2 (certain exceptions are mentioned below). Thus it was known that 2-*O*-acetylresacetophenone (IV) when treated with aluminium chloride gave 4 : 6-diacetylresorcinol (II), but in the isomeric 4-*O*-acetylresacetophenone (V), if the aromatic links are fixed, then the reaction should give 2 : 4-diacetylresorcinol (I); this was actually the main product of the reaction in spite of the complicating factor introduced by the aluminium chloride. The same effect was observed more clearly in the thermal intramolecular rearrangement of the allyl derivatives (VI; R = Me) and (VII; R = Me), the allyl group migrating solely to the positions indicated by the arrows in accordance with expectation, since chelation fixes the bonds in (VI; R = Me), but chelation is prevented in (VII; R = Me) by methylation.[20] Precisely the same result has been obtained with the aldehyde derivatives (VI and VII; R = H) and the propiophenones (VI and VII; R = Et).[21] The direct formation of



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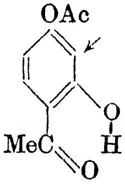
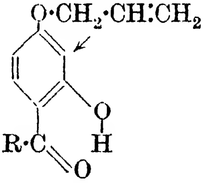
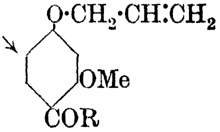


(V.)



(VI.)



(VII.)

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[19] See N. V. Sidgwick, *Ann. Reports*, 1934, **31**, 41; the writer has never stated that a chelate six-membered ring might cause fixation of a double bond by a " Mills–Nixon " strain effect—see G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddel, *J. Amer. Chem. Soc.*, 1936, **58**, 548.

[20] W. Baker and (Miss) O. M. Lothian, *J.*, 1935, 628.

[21] *Idem, ibid.*, 1936, 274.

2 : 4-disubstituted resorcinols (dinitroso, dialdehydo, diacetyl and bisdiazo) may be explained by chelation and by the occurrence of *o*-quinonoid forms.[18]

Infra-red Absorption.—Recent work of more general interest to the study of the interaction of ortho-substituents is that concerned with the infra-red absorption of organic compounds.[22] Organic molecules containing free OH and NH groups show characteristic absorption in the infra-red in the region of 6500—7500 cm.$^{-1}$, and its occurrence may be used to show the presence of such groups in an organic molecule. In certain ortho-substituted phenols, however, this characteristic OH absorption is absent and this may be taken as evidence for the presence of a hydrogen bond in a chelate ring system. In general it is found that compounds which are regarded as being chelated fail to exhibit OH absorption, and that those compounds which cannot form a hydrogen bond do exhibit the expected absorption. For example, the following types of compound do not show OH absorption : β-diketones, *o*-hydroxybenzaldehydes, salicylic esters, *o*-hydroxy-ketones of the benzene, naphthalene and benzophenone series, 1-hydroxyanthraquinones, *o*-nitrophenols, and 2-nitroresorcinol. The following do exhibit OH absorption : β-hydroxybutaldehyde (aldol), α- and β-benzilmonoximes, benzoin, α- and β-benzoinoxime acetates, esters of tartaric acid, catechol and derivatives, guaiacol, *o*-cresol, 1 : 8-dihydroxynaphthalene, *o*-halogenophenols, etc.

According to the American authors the conditions necessary for the formation of a hydrogen bond are (1) the distance between the two oxygen atoms, or the oxygen and the nitrogen atom, sharing the hydrogen bond must be about 2·6 A., (2) the ring should be relatively free from strain, (3) a limited number of bonds in the ring about which there could be freedom of rotation, (4) correct electron affinities of groups sharing hydrogen bonds, (5) the possibility of resonance usually associated with a conjugated system of double bonds. In connection with condition (1) it is interesting to note that *o*-hydroxybenzonitrile (I) exhibits OH absorption, since, owing to the linear nature of the $-C{\equiv}N$ group, the distance N to O is greater than 3 A. and a hydrogen bond cannot be formed. 2-Nitroresorcinol exhibits no OH absorption and thus appears to be doubly chelated (II), a conclusion which was also drawn from its physical properties;[18] structurally analogous is the anion of

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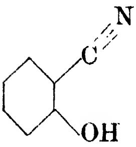
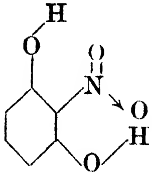
[22] G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddel, *Nature*, 1935, **135**, 147; O. R. Wulf and U. Liddel, *J. Amer. Chem. Soc.*, 1935, **57**, 1464; G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddel, *ibid.*, 1936, **58**, 548, 1991, 2287; J. Errera and P. Mollet, *Compt. rend.*, 1935, **200**, 814; *J. Phys. Radium*, 1935, **6**, 281.

2 : 6-dihydroxybenzoic acid, and the abnormally high dissociation constant of this acid ($K = 5 \times 10^{-2}$) may be due to the double chelation and consequent increased stability of the anion.[23] The non-chelation of aldol is of particular interest in connection with the properties of the isomeric 2 : 4- and 4 : 6-diacetylresorcinols discussed above, but in the case of these actual compounds the conclusions drawn from their infra-red absorption are at variance with the conclusions which have been drawn from a study of other of their physical properties, since neither is stated to exhibit OH absorption bands. There are, moreover, other cases where evidence of chelation drawn from infra-red absorption does not agree with evidence drawn from volatility, solubility, etc.; *e.g.*, by ordinary tests both 2 : 4- and 4 : 6-dinitroresorcinol are but very feebly chelated, but both fail to give OH absorption. It is thus clear that caution must be exercised in accepting the results from infra-red absorption, since absence of characteristic OH absorption might be due to causes other than chelation, *e.g.*, molecular association. Nevertheless, the essential agreement between the conclusions drawn from the usual methods of detecting chelation and from the infra-red absorption is sufficiently close to enable use to be made of the new method in certain structural problems.


(I.)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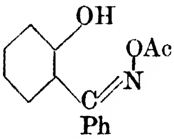
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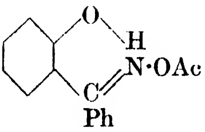
(IV.)

Thus interesting results have been obtained in connexion with the configuration of the oximes. E. P. Kohler and W. F. Bruce[23a] have prepared the two geometrical isomers of 2-hydroxybenzophenoneoxime and their two acetyl derivatives (III) and (IV), and configurations were assigned to the two compounds on the basis of a *trans*-migration of groups during the Beckmann rearrangement. It has now been found[24] that in accordance with this evidence the *syn*-acetate (III) gives the infra-red absorption characteristic of a hydroxyl group, while in the *anti*-acetate (IV) this absorption is absent. Again salicylaldoxime acetate shows no OH absorption, and must possess the *anti*-configuration.

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[23] W. Madelung, *Annalen*, 1922, **427**, 87; W. Baker, *Nature*, 1936, **137**, 236.

[23a] *J. Amer. Chem. Soc.*, 1931, **53**, 1569.

[24] S. B. Hendricks, O. R. Wulf, G. E. Hilbert, and U. Liddel, *ibid.*, 1936, **58**, 1992.

An interesting paper by L. Pauling [25] discusses the interpretation of the infra-red absorption of catechol and related compounds from the point of view that owing to resonance with the benzene ring the C–O link in phenols partakes to a certain extent of the nature of a double bond, so that an ortho-substituted phenol should exist in *cis-* and *trans*-forms with the hydrogen atom lying in the plane of the rest of the molecule. *o*-Chlorophenol is believed to contain about 91% of the *cis*-form owing to the tendency for interaction between the H and Cl atoms. Examples of this type are discussed by O. R. Wulf, U. Liddel, and S. B. Hendricks.[26]

A remarkable case of the alteration of the position taken up by an entering substituent in the benzene nucleus with change in the nature of the entrant radical is recorded by W. A. Silvester and W. P. Wynne.[27] Sulphonation of 2 : 3-dichlorotoluene gives 89% of the 6- and 11% of the 5-sulphonic acid, whilst nitration gives only a 10% yield of the 6-nitro-derivative, and a 90% yield of the 4-nitro-derivative. Another interesting case of orientation is described by P. L. Harris and J. C. Smith,[28] who find that bromination of sodium benzoate with sodium hypobromite at 35° for 7 days gives almost equal quantities of the *o*-, *m*-, and *p*-isomers. This result may be compared with the chlorination of sodium benzoate, where the relative amounts of the isomers are in the order $o > m > p$.[29]

Naphthalene.

The Structure of Naphthalene.—The structure of naphthalene as deduced from its chemical reactions is reviewed by L. F. Fieser and W. C. Lothrop,[30] who conclude that the symmetrical formula, as in (I), is the only one consistent with the experimental evidence. They call attention to familiar facts indicating a double bond between carbon atoms 1 and 2, and a single bond between carbon atoms 2 and 3, such as the reactivity of β-naphthol or β-naphthylamine only in position 1; to the rearrangement of β-naphthyl ally ether to give the 1-allyl derivative, and the failure of the reaction when position 1 is blocked by an alkyl group; to the ring closure of β-substituted naphthalenes at position 1, and to the failure of 2 : 3-dihydroxynaphthalene to yield a quinone on oxidation. Other evidence in favour of a structure (I) is the effect of substituents on the etherification of β-naphthol with an alcohol and a mineral acid,

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[25] *J. Amer. Chem. Soc.*, 1936, **58**, 94.

[26] *Ibid.*, p. 2287.

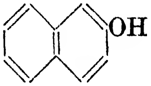
[27] *J.*, 1936, 692.

[28] *Ibid.*, p. 168.

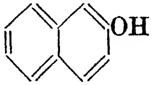
[29] J. C. Smith, *J.*, 1934, 213.

[30] *J. Amer. Chem. Soc.*, 1935, **57**, 1459.

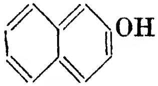
which is prevented by an alkyl group in position 1 but not in position 3, and the refusal of a 1-halogeno-2-naphthol to react normally with halogens, which, instead of attacking position 3, attack the keto-form of the naphthol, again in position 1, to give a ketohalogenide.



(I.)

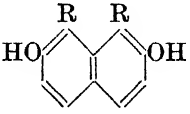


(II.)

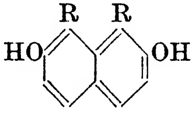


(III.)

These facts may be explained both by the symmetrical structure (I) and also by the unsymmetrical structure (II), although in the latter case it would be difficult to account for the failure of the substance to react in the alternative asymmetrical form (III). In order to obtain an indication of the bond structure of both rings Fieser and Lothrop investigated the behaviour of 2 : 7-dihydroxy-1 : 8-dialkylnaphthalenes (IV). Such compounds completely failed



(IV.)



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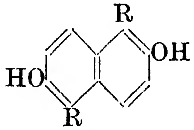

(VI.)

to react with diazotised amines, and their allyl ethers would not undergo thermal rearrangement; such reactions should occur if the asymmetrical structure (V) were a possible one. A similar chemical inertness was found in the 2 : 6-dihydroxy-1 : 5-dialkylnaphthalenes (VI). The authors believe that the reason for the fixed symmetrical distribution of the double bonds in naphthalene is the tendency for each ring to approach as nearly as possible the stable condition of an isolated benzene ring, which must result in the suppression of oscillation. They further regard the enhanced reactivity of the α-positions of naphthalene as probably due to the same causes which are operative in diphenylbutadiene, Ph·CH:CH·CH:CHPh, which is reactive at the two ends of the conjugated aliphatic system, naphthalene being regarded as a benzo-1 : 4-butadiene.

In contrast to this view of the structure of naphthalene V. N. Ufimzev [31] explains the reactivity and the orientation phenomena in naphthalene by assuming an equilibrium between the symmetrical and the asymmetrical form corresponding to (I) and (II).

The results obtained by E. Bergmann and J. Hirshberg [32] on the dissociation constants of naphthoic and chloronaphthoic acids also indicate the inequality of the bonds in the 1 : 2- and the 2 : 3-positions

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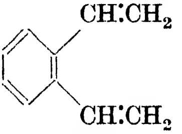
[31] *Ber.*, 1936, **69**, 2188.

[32] *J.*, 1936, 331.

in naphthalene. It was found that the influence of a chlorine atom in the 1-position on the dissociation constant of 2-naphthoic acid is the same as that of a 2-chlorine atom on 1-naphthoic acid. On the other hand, a chlorine atom in position 3 has a smaller influence on the dissociation constant of 2-naphthoic acid.

Evidence of an entirely different nature indicating the presence of a central double bond in naphthalene is afforded by a comparison of some physical properties of *o*-divinylbenzene (VII) and naphthalene.[33] If there is a tendency for the unsaturated side chains to draw one of the nuclear double bonds into conjugation, then of the two possible structures for *o*-divinylbenzene, that shown in (VII) should be the stable form. Comparison of the absorption spectra, molecular refractivities and dispersions of (VII) and naphthalene shows that the compounds are remarkably similar, and differ appreciably from α-phenylbutadiene. Similarly benzene is spectrochemically very different from $\Delta^{\alpha\gamma\epsilon}$-hexatriene. The authors conclude that no " optical neutralisation of valencies " takes place in passing from (VII) to naphthalene. According to K. W. F. Kohlrausch [34] the infra-red and the Raman spectra of naphthalene are in harmony with symmetrical structures such as in (I), but not with unsymmetrical structures as in (II).



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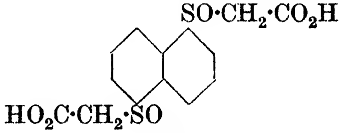

(VIII.)

Evidence as to the structure of naphthalene from dipole moment measurements, however, is inconsistent with any molecule containing rigid bonds. G. C. Hampson and A. Weissberger [35] have measured the dipole moments of α- and β-chloronaphthalene, and the ten isomeric dichloronaphthalenes. Both 1 : 5- and 2 : 6-dichloronaphthalene have zero moments, but 1 : 4-dichloronaphthalene has a moment of 0·48 D, which is interpreted as being due to an induced moment in the molecule at right angles to the C–Cl bonds, which are regarded as directed from the centre of the ring. They conclude that, if there is any fixation of the single and double bonds in naphthalene, it is not revealed in the direction of the substituents.

A neat confirmation of the equivalence of the 1- and the 5-position in naphthalene, which must also be assumed to possess a centre of symmetry, is afforded by the preparation of naphthalene-1 : 5-di-

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[33] K. Fries, H. Bestian, and W. Klauditz, *Ber.*, 1936, **69**, 715.

[34] *Ber.*, 1935, **68**, 893.

[35] *J.*, 1936, 393.

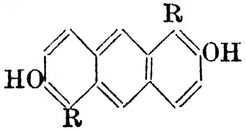
sulphinylacetic acid (VIII) in a *meso*- and a racemic form, the centres of asymmetry being the sulphur atoms.[36]

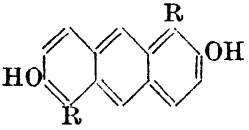
A detailed study of the sulphonation of naphthalene has been carried out by R. Lantz.[37] This commercially important reaction, first studied systematically by V. Merz and W. Weith in 1870,[38] yields mainly either the α- or the β-acid according to the experimental conditions. The transformation of the α- into the β-acid is shown to be due to the fact that, although both acids are formed in the sulphonation, the α-acid is hydrolysed some fifty times more quickly than the β-acid, and this difference between the two acids becomes more marked with rise of temperature and/or concentration of sulphuric acid, so that increase in temperature or in concentration of acid favours the production of the β-sulphonic acid. With sulphuric acid of the correct strength under the appropriate conditions it is possible to hydrolyse the α-sulphonic acid to naphthalene without causing β-sulphonation.

Anthracene.

L. F. Fieser and W. C. Lothrop[39] have extended their work on the structure of naphthalene to the case of anthracene. They are of the opinion that there is no valid evidence to show that anthracene is not composed of rings of the Kekulé type, and they have attempted to decide between the two possible structures, which would possess the arrangements of bonds shown in (I) and (II).

(I.)





(II.)

Structure (I) was regarded as the more probable owing to its more completely aromatic character. The 1 : 5-dimethyl and 1 : 5-diallyl derivatives of 2 : 6-dihydroxyanthracene were prepared (I and II; R = Me and C_3H_5) and their power to couple with diazotised bases was investigated. If they possess structure (I), which contains no ortho-position doubly bound to the hydroxylated carbon atoms, they should be incapable of coupling with diazotised amines, but if they possess structure (II) or if the bond structure is capable of tautomeric change to (II), then coupling should occur. Experiment showed that both these 1 : 5-dialkyl-2 : 6-dihydroxyanthracenes were incapable of coupling reactions, and the authors conclude that anthracene possesses the immobile bond system (I).

[36] F. Gazowczyk and J. Susko, *Bull. Acad. Polonaise*, 1935, *A*, 349.

[37] *Bull. Soc. chim.*, 1935, [v], 2, 2092.

[38] *Ber.*, 1870, 3, 195.

[39] *J. Amer. Chem. Soc.*, 1936, 58, 749.

Aromatic Deuterium Compounds.

Hexadeuterobenzene was first prepared by polymerisation of dideuteroacetylene,[40] the reaction being conveniently catalysed by tellurium.[41] It has also been prepared from benzene by interaction with deuterium oxide in presence of nickel,[42] and from benzene and deuterium chloride in presence of aluminium chloride.[43] A further method is the decomposition of calcium mellitate with calcium deuteroxide.[44]

The transference of deuterium to benzene without the use of heterogeneous catalysts was first recorded by C. K. Ingold, C. G. Raisin, and C. L. Wilson,[45] who found that a ready exchange of hydrogen for deuterium took place when benzene was treated with heavy sulphuric acid. Further details of the method have now been recorded [2] in connexion with the preparation of hexadeuterobenzene containing hydrogen corresponding to only 1% of pentadeuterobenzene. Pure benzene is shaken for 3—4 days with a solution of heavy sulphuric acid in heavy water containing 51 mols. % of heavy acid. Under these conditions a small amount of sulphonation takes place, but with an acid of 40 mols. % strength sulphonation is entirely avoided and yet the exchange still occurs, though at a lower rate.

Hexadeuterobenzene differs appreciably from benzene in its physical properties.

	M. p.	B. p.	$d_{25^\circ}^{25^\circ}$.	$d_{4^\circ}^{25^\circ}$.	$n_D^{22^\circ}$.
Hexadeuterobenzene	6·8°	79·3°	0·9456	0·9429	1·49779
Benzene	5·5°	80·1°	0·8760	0·8735	1·49982

Its vapour pressure is slightly greater than that of benzene.

With regard to the mechanism of the exchange employed by Ingold and his co-workers it is definitely shown that it does not consist in successive sulphonation and desulphonation, since a small portion of partly deuterated benzenesulphonic acid (normal with respect to the hydrogen isotope in the sulphonic acid group), when introduced into an exchange experiment with "light" benzene and "light" sulphuric acid, did not result in the equilibrium benzene

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[40] J. W. Murray, C. F. Squire, and D. H. Andrews, *J. Chem. Physics*, 1934, **2**, 714.

[41] G. R. Clemo and A. McQuillen, *J.*, 1935, 851.

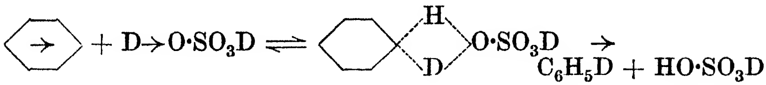
[42] P. I. Bowman, W. S. Benedict, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1935, **57**, 960.

[43] A. Klit and A. Langseth, *Z. physikal. Chem.*, 1936, **176**, 65.

[44] H. Erlenmeyer and H. Lobeck, *Helv. Chim. Acta*, 1935, **18**, 1464; H. Erlenmeyer, H. Lobeck, H. Gärtner, and A. Epprecht, *ibid.*, 1936, **19**, 336.

[45] *Nature*, 1934, **134**, 734.

containing any more than the normal amount of deuterium. These authors formulate the exchange in the following way,



involving a one-point addition[46] and not a two-point addition as postulated by J. Horiuti and M. Polanyi.[47] Polarisation of the benzene nucleus is supposed to take place and also polarisation of the sulphuric acid in a direction corresponding to the normal ionisation of the acid, the resulting reaction being undetectable except by the use of an isotopic indicator. The "abnormal" polarisation of the sulphuric acid $HO \leftarrow SO_3H$ is involved in the ordinary process of sulphonation. This exchange mechanism requires that the deuteration of substituted benzenes by acidic reagents should follow the familiar rules for orientation and velocity in aromatic substitution, and should take place the more readily with increase in the proton- or deuteron-donating power of the reagent.[48] These requirements are borne out by experiment. With regard to the latter point the deuterating powers of reagents should be in the order $D_2SO_4 > D_3\overset{+}{O} > DOAc > D_2O$, which is actually found. With benzene exchange only takes place with the first, with anisole with both the first and the second. With anisole the exchange proceeds at first very rapidly but only with respect to three positions, probably the two *o*- and the *p*-hydrogen atoms, and thereafter at a very much slower rate. With phenol one hydrogen atom, doubtless that of the hydroxyl group, is rapidly exchanged with water alone,[49] and in presence of alkali three more hydrogen atoms, presumably those of the *o*- and *p*-positions, become exchangeable.[49a]

Such exchange reactions should afford a valuable method for the estimation of active hydrogen atoms in organic compounds[50] when sufficient preliminary work has been carried out with compounds of known structure. In this connexion the results obtained by F. K. Münzberg[51] in the exchange reaction between polyhydroxy-

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[46] *Idem*, *Nature*, 1934, **134**, 847.

[47] *Ibid.*, p. 847.

[48] C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J.*, 1936, 1637.

[49] See M. Harada and T. Titani, *Bull. Chem. Soc. Japan*, 1935, **10**, 554; 1936, **11**, 465.

[49a] See also P. A. Small and J. H. Wolfenden, *J.*, 1936, 1811.

[50] See H. Erlenmeyer, A. Epprecht, H. Lobeck, and H. Gärtner, *Helv. Chim. Acta*, 1936, **19**, 354; H. Erlenmeyer, A. Epprecht, and H. Lobeck, *ibid.*, p. 543.

[51] *Z. physikal. Chem.*, 1936, *B*, **33**, 23, 39.

benzenes and heavy water are of considerable interest. In the case of resorcinol the two hydrogen atoms of the hydroxyl groups are immediately replaced by deuterium, followed by a much slower exchange of two further hydrogen atoms, and there is little indication of further reaction. This same degree of displacement occurs in about one-eightieth of the time in *N*/10-alkaline solution. The behaviour of orcinol is similar. The author suggests that in these two compounds the double bonds are fixed and that the two nuclear hydrogen atoms are replaced by way of an enol-keto transformation. Such a conclusion is difficult to reconcile with the well-known reactivity of resorcinol,[18] which normally undergoes substitution with extreme ease in positions 4 and 6, and finally 2, the formation of such products requiring the alternation of the double bonds. It is remarkable that three nuclear hydrogen atoms are not replaced with almost equal ease. In the case of quinol the rapid replacement of the two hydroxylic hydrogen atoms is followed by a very slow replacement of all four remaining hydrogen atoms, the reaction being appreciably hastened in *N*/10-alkaline solution, this observation being parallel with the known reactivity of the quinol nucleus; there seems no good reason for believing with the author that there are only two double bonds in the nucleus of quinol. In the case of pyrogallol the rapid replacement of the three hydroxylic hydrogen atoms is followed by a slower exchange of two of the nuclear hydrogen atoms, and in phloroglucinol all six hydrogen atoms are rapidly replaced; both these results are to be expected.

The equilibrium between aniline hydrochloride and heavy water is established at 60° after 3 hours with production of $C_6H_2D_3{\cdot}ND_3Cl$.[52] Ready exchange of one hydrogen atom occurs in aniline, pyrrole, benzoic acid, and benzyl alcohol.[53] Crystallisation of the nitrates of strychnine and vomicine from deuterium oxide indicates the presence of one and three replaceable hydrogen atoms respectively, one of which is, of course, the hydrogen of the nitric acid in each case, so that strychnine itself contains no replaceable hydrogen atoms, and vomicine contains two.[54] Other results found by the exchange method are that barbituric acid contains four replaceable hydrogen atoms, and phenacetin contains one.[55]

Pentadeuterobenzoic acid has been prepared from hexadeuterobenzene through the stages pentadeuterobromobenzene and penta-

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[52] M. Harada and T. Titani, *Bull. Chem. Soc. Japan*, 1936, **11**, 554.

[53] *Idem*, *ibid.*, 1936, **11**, 465.

[54] H. Erlenmeyer, A. Epprecht, and H. Lobeck, *Helv. Chim. Acta*, 1936, **19**, 543; cf. Zerewitinoff determination, H. Wieland and F. Hölscher, *Annalen*, 1933, **500**, 70.

[55] H. Erlenmeyer, H. Lobeck, and H. Gärtner, *Helv. Chim. Acta*, 1936, **19**, 354.

deuterophenylmagnesium bromide;[56] its melting point is 0·8° lower than that of benzoic acid, and its solubility in water 0·06 g. in 100 c.c. of water at 18° greater than that of benzoic acid. Two methods are available for the preparation of partly deuterated benzenes of known orientation; the first is the distillation of the calcium salts of the appropriate benzenecarboxylic acids with calcium deuteroxide, by which method monodeuterobenzene,[57] *o*- and *m*-dideuterobenzenes,[58] and 1 : 3 : 5-trideuterobenzene [59] have been prepared, and the second is by the deuteration of a substituted benzene, giving a partly deuterated product of known orientation, and subsequent elimination of the original group.

W. B.

5. DEHYDROGENATION IN THE DETERMINATION OF STRUCTURE.

The use of dehydrogenation * in the examination of natural products of complex hydroaromatic structure has increased very greatly during the past fifteen years, and many results obtained in this way have been recorded in these Reports. During this period information has gradually been accumulating on the control of the various dehydrogenation processes by the study of substances of known structure. A large and scattered literature on this subject has grown up, and it seems advisable at the present state of development to attempt a connected account, although there are still many problems unsettled. The literature is in some respects conflicting, owing, no doubt, to differences in the experimental conditions used by various investigators and (in the case of catalytic dehydrogenation) to variations in the method of preparation of the catalyst. Some of the conclusions stated below are therefore tentative, but they serve to indicate the present limitations of the method.

The principal dehydrogenating agents are (1) sulphur, (2) selenium, (3) catalytic metals. Other methods, such as exhaustive bromination [1] and the use of manganese dioxide and acid,[13] have not found general application.

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[56] H. Erlenmeyer, H. Lobeck, and A. Epprecht, *Helv. Chim. Acta*, 1936, **19**, 793; H. Erlenmeyer and A. Epprecht, *ibid.*, p. 1056.

[57] N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, 1935, **10**, 557.

[58] O. Redlich and W. Stricks, *Monatsh.*, 1936, **68**, 47, 374.

[59] L. H. P. Weldon and C. L. Wilson, *Nature*, 1936, **137**, 70.

[1] See, *e.g.*, A. von Baeyer and V. Villiger, *Ber.*, 1899, **32**, 2429.

* The term " dehydrogenation " is limited in this section to the conversion of alicyclic compounds into their aromatic counterparts by removal of hydrogen (and also in some cases of other atoms or groups). This is the only reaction involving dehydrogenation which has been generally used for the determination of structure.

(1) *Sulphur.*

Normal Dehydrogenations.[2]—The early work has been reviewed by L. Ruzicka.[3] The formation of aromatic hydrocarbons from natural products by heating with sulphur was first observed by Paul Curie [4] and W. Kelbe [5] for colophony and by A. Vesterberg [6] for purified abietic acid (which yielded retene), and W. B. Markownikoff and J. Spady [7] had obtained *m*-xylene from a petroleum ' naphthene.' The first dehydrogenation of a pure compound of known structure by sulphur was the preparation of naphthalene from tetralin, mentioned by J. von Braun and G. Kirschbaum.[8] The main development of the subject commenced with the work of L. Ruzicka on the dehydrogenation of the sesquiterpenes. As is well known, it was found [9, 10] that all the known dicyclic sesquiterpenes could be converted by the action of sulphur at about 200° into one of two derivatives of naphthalene, either cadalene ($C_{15}H_{18}$) or eudalene ($C_{14}H_{16}$). The structure of these was shown by their synthesis.[11] In control experiments, it was shown that the simple terpenes, limonene and terpinene, on similar treatment gave *p*-cymene,[12] so that there was no rearrangement of the carbon skeleton. It is significant that the yield of *p*-cymene from terpinene, in which both double bonds are contained in the *cyclo*hexane ring, is greater than that from limonene, in which one double bond is exocyclic (50 against 15%). The formation of *p*-cymene from limonene involves an effective *hydrogenation* of the *iso*propenyl side chain, accompanying the dehydrogenation of the ring. We shall return to this point later.

In 1927, L. Ruzicka and E. A. Rudolph [13] noted that dehydrogenation of tetralin with sulphur gave a 70% yield of naphthalene. In general it appeared that the further removed a compound was from the aromatic state, the lower was the yield on dehydrogenation. Thus dihydronaphthalenes were very easily dehydrogenated,[3] but the fully hydrogenated tetrahydrocadinene (I) yielded no aromatic hydrocarbon on treatment with sulphur at 200—260°.[10] Similarly,

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[2] *I.e.*, those in which no carbon-to-carbon bond is broken or formed.

[3] *Fortschritte der Chem. Phys.*, 1928, **19**, Heft 5, 1.

[4] *Chem. News*, 1874, **30**, 189.

[5] *Ber.*, 1878, **11**, 2174.

[6] *Ibid.*, 1903, **36**, 1903.

[7] *Ibid.*, 1887, **20**, 1850.

[8] *Ibid.*, 1921, **54**, 609.

[9] L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, 1921, **4**, 505.

[10] L. Ruzicka, J. Meyer, and M. Mingazzini, *ibid.*, 1922, **5**, 345.

[11] L. Ruzicka and C. F. Seidel, *ibid.*, p. 369; L. Ruzicka and M. Stoll, *ibid.*, p. 923.

[12] Compare G. Austerweil and L. Penfaillit, G.P. 414,912 of 1925.

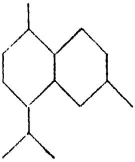
[13] *Helv. Chim. Acta*, 1927, **10**, 915.

R. Weiss and K. Woidich [14] found that 1-(1′-naphthyl)*cyclo*hexene (II) gave 1-phenylnaphthalene readily on treatment with sulphur, whereas J. W. Cook and C. A. Lawrence obtained only a poor yield from the corresponding saturated hydrocarbon.[15] M. D. Bodroux [16] has successfully dehydrogenated 2-*cyclo*hexylnaphthalene with sulphur to 2-phenylnaphthalene, so that the presence of an (unfused) aromatic ring may assist the reaction.

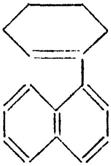
The general technique of the process is described by L. Ruzicka.[3] It is customary to use only the theoretical amount of sulphur required to bring the compound to the aromatic state; thus, for a sesquiterpene,

$$C_{15}H_{24} + 3S \longrightarrow C_{15}H_{18} + 3H_2S$$

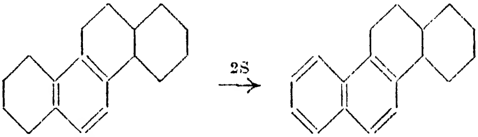
By the use of a deficiency of sulphur a partial dehydrogenation can be achieved. Thus J. von Braun and G. Irmisch converted dodecahydrochrysene (III) into octahydrochrysene [17] (IV).



(I.)



(II.)



(III.) (IV.)

The reaction is usually carried out at a temperature of 180° to 250°, without a solvent, but naphthalene has been used as a solvent in the dehydrogenation of *cyclo*hexanone,[18] and quinoline in that of tetrahydrobenzpyrene.[19]

Recently the principal applications of sulphur in dehydrogenation have been to oxygenated compounds. G. Darzens and his collaborators [20] have used it widely for the conversion of carboxylic acids derived from tetralin and tetrahydrophenanthrene into the aromatic state. These dehydrogenations were usually carried out under reduced pressure. The carboxyl group was not generally affected, but in the case of 1-methyltetralin-4-carboxylic acid it was eliminated with the formation of 1-methylnaphthalene.[21] L. F. Fieser and E. B. Hershberg observed a particularly rapid dehydrogenation of the anhydrides of dihydronaphthalene- and dihydrophenanthrene-*o*-

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[14] *Monatsh.*, 1925, **46**, 456.

[15] *J.*, 1936, 1431.

[16] *Ann. Chim.*, 1929, [x], **11**, 511.

[17] *Ber.*, 1932, **65**, 883.

[18] G. Darzens and G. Lévy, *Compt. rend.*, 1932, **194**, 181.

[19] A. Winterstein, H. Vetter, and K. Schön, *Ber.*, 1935, **68**, 1079.

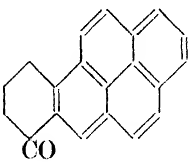
[20] See p. 326.

[21] G. Darzens and A. Lévy, *Compt. rend.*, 1934, **199**, 1131.

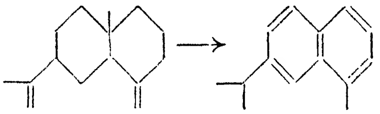
dicarboxylic acids.[22] Various dehydrogenations by means of sulphur of hydroaromatic acids containing the carboxyl group at the end of a side chain have been recorded.[23, 24] G. Haberland [24] reports a reaction in which the use of an equivalent amount of sulphur gives a nearly quantitative yield, but some sulphur remains unattacked; it is suggested that the action may be partly catalytic. On the other hand, L. Ruzicka and E. A. Rudolph [13] observed a complete decomposition of the sulphur in the dehydrogenation of tetralin.

The dehydrogenation of ketones without secondary decomposition is more difficult than that of acids, as there is a simpler path for the elimination of the oxygen. G. Darzens and G. Lévy,[18] however, have succeeded in preparing phenol and α-naphthol from *cyclo*hexanone and α-tetralone respectively, and L. F. Fieser, E. B. Hershberg, and M. S. Newman [25] obtained a 19% yield of pure hydroxybenzpyrene by the rapid action of sulphur on the ketone (V). Esters have been successfully dehydrogenated by the same two schools,[26] and an aromatic methoxyl group has been found to be unaffected by sulphur dehydrogenation.[22, 24, 26]

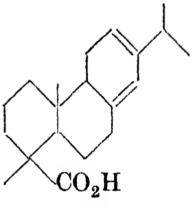
Abnormal Dehydrogenations.—As is well known, in the dehydrogenation of selinene (VI) and the corresponding alcohol, eudesmol, one carbon atom is eliminated from the molecule, with the production of 1-methyl-7-*iso*propylnaphthalene (eudalene, VII) in place of the dimethyl*iso*propylnaphthalene (cadalene) obtained from the cadinene group of sesquiterpenes. Ruzicka [10, 11] interpreted this as an elimination of a quaternary methyl group as methyl mercaptan and placed this labile methyl group in the angular position (as in VI).



(V.)



(VI.) (VII.)



(VIII.)

Here again the unsaturated side chains become reduced during the dehydrogenation. A similar change is believed to underlie the

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[22] *J. Amer. Chem. Soc.*, 1935, **57**, 1851; compare L. F. Fieser and H. L. Holmes, *ibid.*, 1936, **58**, 2319.

[23] N. N. Chatterjee, *J. Indian Chem. Soc.*, 1935, **12**, 591; I. R. Sherwood, W. F. Short, and J. Woodcock, *J.*, 1936, 322.

[24] G. Haberland, *Ber.*, 1936, **69**, 1380.

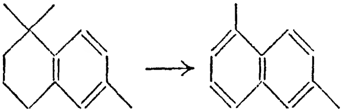
[25] *J. Amer. Chem. Soc.*, 1935, **57**, 1509.

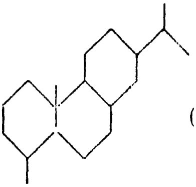
[26] G. Darzens and A. Lévy, *Compt. rend.*, 1935, **200**, 469; L. F. Fieser and (Mrs.) M. Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 1679.

conversion of abietic acid (probably VIII) into retene (1-methyl-7-*iso*propylphenanthrene).[6, 27] So far the elimination of an angular methyl group by sulphur dehydrogenation of a synthetic compound of known structure does not appear to have been accomplished. Ruzicka and Rudolph [13] have, however, shown that ionene (IX) eliminates one methyl group from its quaternary carbon atom to give 1 : 6-dimethylnaphthalene. The yield (10%) is similar to that of cadalene from the eudesmol group of sesquiterpenes. The yield of aromatic hydrocarbon is generally lower with these more complicated reactions. As Ruzicka failed to detect the presence of lower homologues from normal dehydrogenations, he concludes that the elimination of methyl only occurs from a quaternary carbon atom, when otherwise dehydrogenation would not be possible.

The fichtelite (X) of fossil resins yielded retene with sulphur at 180—250°, with elimination of a methyl group.[27] The dehydrogenation of this compound is noteworthy, as it is fully saturated. Curiously enough, it is reported [28] that 1 : 1-dimethyltetralin, the lower homologue of (IX), is not dehydrogenated by sulphur at 221°.

(IX.)





(X.)

Turning from the breaking of carbon bonds to their formation under the conditions of sulphur dehydrogenation, it may be noted that the monocyclic zingiberene (XI) readily yields cadalene (XII).[10, 29] Such cyclisations are uncommon; the isomeric bisabolene shows no sign of yielding a naphthalene derivative under the same conditions.[29] The majority of tricyclic sesquiterpenes also are not dehydrogenated to naphthalene derivatives; [30] an exception is copaene, which yields cadalene with sulphur.[31] Ruzicka correlates the tendency of mono- and tri-cyclic sesquiterpenes to yield naphthalene derivatives on sulphur dehydrogenation with their ability to isomerise readily into hydronaphthalenes on treatment with acids.[3]

An even more remarkable ring closure was that observed by

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[27] L. Ruzicka, F. Balas, and H. Schinz, *Helv. Chim. Acta*, 1923, **6**, 692.

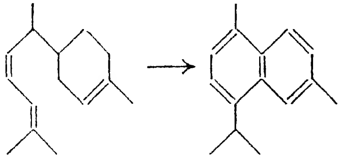
[28] M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *J. Amer. Chem. Soc.*, 1934, **56**, 959.

[29] L. Ruzicka and A. G. van Veen, *Annalen*, 1929, **468**, 133.

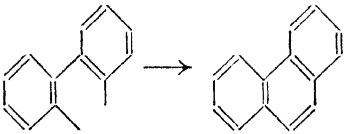
[30] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1923, **6**, 853; G. G. Henderson, R. O. O. McCrone, and J. M. Robertson, *J.*, 1929, 1368.

[31] G. G. Henderson, W. M'Nab, and J. M. Robertson, *J.*, 1926, 3077.

H. Berger,[32] who prepared phenanthrene by heating di-*o*-tolyl (XIII) with sulphur at 250°.



(XI.) (XII.)



(XIII.)

An unusual rearrangement of the carbon skeleton would appear to underlie the formation of phenanthrene by sulphur dehydrogenation of 1-*cyclo*pentylhydrindene.[33]

(2) *Selenium.*

The discovery that selenium could be used in place of sulphur for dehydrogenations is due to O. Diels, who in 1927 published an account of the action of this reagent on cholesteryl chloride and cholesterol.[34] There is a general resemblance between the behaviour of sulphur and selenium, but the new reagent gives, on the whole, better yields and less side-reaction. The temperature used in selenium dehydrogenation is invariably higher than that used with sulphur, 280—350° being the usual range. Higher temperatures, as will be seen, may cause rearrangements.

O. Diels and (Frl.) A. Karstens[35] reported that selenium was preferable to sulphur for the dehydrogenation of cadinene to cadalene, and of abietic acid to retene; and could also be applied to the preparation of triphenylene from its dodecahydro-derivative. L. Ruzicka and A. G. van Veen[36] also found that selenium was able to convert elemol and elemene into eudalene, which was not possible by the use of sulphur, and the new reagent rapidly passed into general use for the dehydrogenation of both natural and synthetic substances.

Normal Dehydrogenations.—It was soon found that synthetic hydroaromatic compounds containing no quaternary carbon atoms passed very readily into their aromatic counterparts. The yields were good, particularly when the compounds already contained one or more aromatic rings. The evidence on these points comes mainly from the work of L. Ruzicka, R. D. Haworth, I. M. Heilbron, J. W. Cook, R. Robinson, and their co-workers and need not be detailed.

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[32] *J. pr. Chem.*, 1932, [ii], **133**, 331; compare W. F. Short, H. Stromberg, and A. E. Wiles, *J.*, 1936, 319.

[33] R. Robinson, *J.*, 1936, 80; J. D. Fulton and R. Robinson, *J.*, 1933, 1463.

[34] O. Diels, W. Gädke, and P. Körding, *Annalen*, 1927, **459**, 1.

[35] *Ber.*, 1927, **60**, 2323.

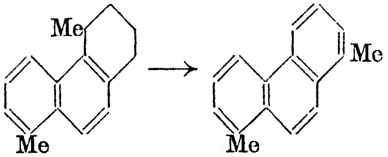
[36] *Annalen*, 1929, **476**, 70.

As in the case of sulphur, fully saturated rings resist dehydrogenation. For example, (*trans*-)decalin was practically unaffected by selenium at 340—360°, but yielded naphthalene at 370—390°,[37] and 2-benzyl-*trans*-decalin was not dehydrogenated at 320—330° [38] (in contrast, 2-benzyl-*trans*-octalin yielded 2-benzylnaphthalene in very good yield at 320°).[38, 39] 2-Methyldecalin gave a poor yield of 2-methylnaphthalene at 320—350°.[40]

Cholestane and perhydrocalciferol were stable to selenium at 300—320° and cholestane was only partly dehydrogenated at 340—350°.[38] Perhydrophenanthrene was not dehydrogenated at 300—320°.[41] It appears, therefore, that most fully saturated compounds are first dehydrogenated by selenium at about 350° and that this critical temperature varies slightly with different compounds. When a fully reduced *cyclo*hexane ring is present in a molecule containing an aromatic ring, the loss of hydrogen is often easier. Thus, hexahydrofluorene [38] and 2-*cyclo*hexylnaphthalene [42] both yield the corresponding aromatic substances with selenium at 300—320°.

If dehydrogenation is to give a reliable diagnosis of structure, it is fundamentally important that alkyl groups (other than those attached to quaternary carbon atoms) should not migrate or be eliminated during the reaction. This is generally true, as is shown, for example, by the fact that many alkyl naphthalenes and phenanthrenes made by processes involving a final selenium dehydrogenation are identical with those synthesised by other methods. Nevertheless, it would be premature to consider the non-migration of alkyl groups as fully proved. Conflicting results have been discovered by R. D. Haworth, C. R. Mavin, and G. Sheldrick.[43] For example, the hydrocarbon (XIV), prepared by an apparently unequivocal method, yielded mainly 1 : 8-dimethylphenanthrene (XV) and only a little of the expected 1 : 5-isomeride. Some of the re-

(XIV.)



(XV.)

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[37] L. Ruzicka and C. F. Seidel, *Helv. Chim. Acta*, 1936, **19**, 424.

[38] J. W. Cook and C. L. Hewett, *J.*, 1936, 70.

[39] J. W. Barrett and R. P. Linstead, *J.*, 1936, 611.

[40] J. W. Barrett, A. H. Cook, and R. P. Linstead, *J.*, 1935, 1065.

[41] P. S. Pinkney, G. A. Nesty, R. H. Wiley, and C. S. Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 972.

[42] J. W. Cook and C. A. Lawrence, *J.*, 1936, 1431.

[43] *J.*, 1934, 454.

arrangements occurred with material prepared by the Bardhan–Sengupta method (see p. 304). In such cases it is possible to explain the discrepancies as being due to rearrangement at the stage of dehydration during the synthesis; but this explanation is not generally valid and there is no direct evidence in its favour. All the migrations observed by Haworth, Mavin, and Sheldrick were from the 4- to the 1-carbon atom, during the dehydrogenation of a tetrahydrophenanthrene (such as XIV), but the exact structural requirements are unknown. L. Ruzicka, K. Hofmann, and J. Frei [44] state that during selenium (and palladium) dehydrogenation up to 350°, no alkyl migrations have been observed from the 1- to the 2-position in naphthalene, or from the 3- to the 4-position in phenanthrene, providing no neighbouring substituent is eliminated.

L. Ruzicka and co-workers have examined the behaviour of a number of simple cyclic hydrocarbons containing rings other than 6-membered.[45, 37] It was found that derivatives of hydrindene, *cyclo*heptane and *cyclo*octane resisted the action of selenium at 350°, although rearrangements occurred at higher temperatures (see below). It is clear that evidence obtained from dehydrogenation above 350°, though it may be of some service, must be interpreted with discretion. Even this temperature is dangerously close to that (*ca.* 420°) which enables alkyl groups to migrate from the α- to the β-position in naphthalene, over such catalysts as silica gel; and phenyl groups migrate even at 350°.[45a]

Two side reactions may be mentioned. The hydrogenation of unsaturated side chains, or of cyclic double bonds, by the action of selenium at high temperatures has been frequently observed, *e.g.*, in experiments on oleanolic acid,[46] cholesterilene,[47] hydrocarbons containing allyl side chains,[48] and various indenes.[45] These reductions probably result from a disproportionation of hydrogen, similar to that observed with 1-naphthyl*cyclo*hexene, which gives a mixture of phenyl- and *cyclo*hexyl-naphthalenes on treatment with selenium.[42] J. von Braun and G. Irmisch [17] observed a partial dehydrogenation of dodecahydrochrysene with selenium at 320°, and J. W. Cook and C. L. Hewett obtained a mixture of 1 : 2-benzanthracene and a tetrahydro-derivative similarly from dodecahydrobenzanthracene.[49]

[44] *Helv. Chim. Acta*, 1936, **19**, 386.

[45] L. Ruzicka and E. Peyer, *ibid.*, 1935, **18**, 676.

[45a] F. Mayer and R. Schiffner, *Ber.*, 1934, **67**, 67.

[46] L. Ruzicka, H. Hösli, and L. Ehmann, *Helv. Chim. Acta*, 1934, **17**, 442.

[47] C. Dorée and V. A. Petrow, *J.*, 1934, 1129.

[48] A. Cohen, J. W. Cook, and C. L. Hewett, *J.*, 1935, 1633; J. W. Cook and G. A. D. Haslewood, *ibid.*, p. 767.

[49] *J.*, 1934, 370.

Abnormal Dehydrogenations.—The selenium dehydrogenation of various sterols [34, 35] leads to the well-known $C_{18}H_{16}$ hydrocarbon of Diels, now known to be 3-methyl*cyclo*pentenophenanthrene. The dehydrogenation of cholic acid according to O. Diels and A. Karstens [35] yielded chrysene, whereas L. Ruzicka and his collaborators obtained the $C_{18}H_{16}$ hydrocarbon.[50] There were further differences between the observations of the two schools on the composition of the pentacyclic compounds isolated as by-products. From the available evidence,[51] it appears that the differences must be due to the higher temperatures involved in the experiments of Diels; for Ruzicka and co-workers obtained chrysene from cholic and cholatrienic acids readily at 420°. The following changes are involved in these selenium dehydrogenations: elimination of one angular methyl group, elimination of the long side chain from C_{17} (sterol numbering), and migration to this atom of the second angular methyl group (from C_{13}). For the formation of chrysene a ring enlargement from 5- to 6-carbon must occur. We shall consider below how far these reactions are paralleled among synthetic compounds of known structure.

In Ruzicka's experiments, already mentioned,[37, 45] it was found that α- and β-methylhydrindenes yielded naphthalene with selenium at 450°. Curiously enough, hydrindenes with more complex side chains also gave naphthalene, not alkylnaphthalenes, but in worse yield (palladised charcoal gave similar results). *cyclo*-Heptane and -octane yielded toluene and *p*-xylene at 440° and 400° respectively. Obviously the results with α-methylhydrindene provide a model for the formation of chrysene in place of methyl*cyclo*pentenophenanthrene in dehydrogenations of bile acids and sterols. The elimination of an angular methyl group by selenium at the customary temperatures (*ca.* 320°) has been substantiated with the synthetic compounds prepared by G. A. R. Kon, J. W. Cook, L. Ruzicka, and their co-workers.[52] C. K. Chuang, V. L. Tien, and C. M. Ma have converted 9-methyloctalin into naphthalene with selenium at 430°.[53] Fully saturated dicyclic compounds containing quaternary carbon atoms resist selenium dehydrogenation at about 300—350°,[53, 54] but ionene gives a good yield of 1 : 6-dimethylnaphthalene with elimination of a methyl group.[54]

[50] L. Ruzicka and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 216; L. Ruzicka, M. W. Goldberg, and G. Thomann, *ibid.*, p. 812.

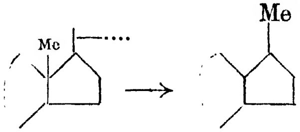
[51] L. Ruzicka, G. Thomann, E. Brandenberger, M. Furter, and M. W. Goldberg, *ibid.*, 1934, **17**, 200; L. Ruzicka and M. W. Goldberg, *ibid.*, 1935, **18**, 434; cf. O. Diels and H. Klare, *Ber.*, 1934, **67**, 113.

[52] For references, see p. 323 *et seq.*

[53] *Ber.*, 1936, **69**, 1494.

[54] G. R. Clemo and H. G. Dickenson, *J.*, 1935, 735.

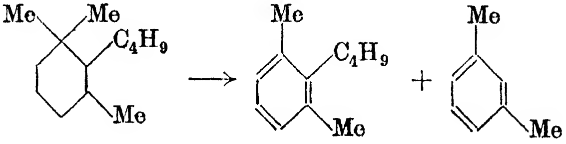
The remaining feature of the dehydrogenation of the sterols and bile acids is the change in ring D which may be symbolised:



There is every reason to believe that the migration of the methyl group is closely bound up with the elimination of the side chain,[55] but no synthetic compounds are as yet available which will provide exact comparison. In the degradation of natural products L. Ruzicka has observed the migration of a methyl group to accompany the elimination of a neighbouring hydroxyl. Such a change must account for the formation of sapotalin (1 : 2 : 7-trimethylnaphthalene) in the dehydrogenation of the pentacyclic triterpenes.[46, 56] Another example of a methyl migration has been encountered in the degradation of alantolactone,[57] but in this case it is probably independent of dehydrogenation.

Several examples of the formation of new rings under the conditions of selenium dehydrogenation have been observed, but usually only at very high temperatures. Thus 1 : 2-diethyl*cyclo*hexene yielded naphthalene at 420°,[45] whereas 1 : 1 : 3-trimethyl-2-*n*-butyl*cyclo*hexane (XVI) at 390—400° reacted as follows:[37]

(XVI.)



(The elimination of the large side chain *without* migration of a neighbouring tertiary methyl group is noteworthy.) A more complicated example is the formation of pentacyclic hydrocarbons in the dehydrogenation of sterols and bile acids;[34, 35, 50, 51] this is a secondary reaction due to the presence of the labile side chain.[58]

An interesting rearrangement was realised by G. R. Clemo and J. Ormston in the dehydrogenation of the *spiro*-ketone (XVI*a*) and

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[55] See, *e.g.*, A. Cohen, J. W. Cook, and C. L. Hewett's study of the reaction (*J.*, 1935, 448).

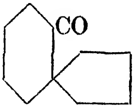
[56] L. Ruzicka, K. Hofmann, and J. Frei, *Helv. Chim. Acta*, 1936, **19**, 386; L. Ruzicka, K. Hofmann, and H. Schellenberg, *ibid.*, p. 1391.

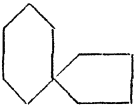
[57] L. Ruzicka, P. Pieth, T. Reichstein, and L. Ehmann, *ibid.*, 1933, **16**, 268.

[58] J. W. Cook, C. L. Hewett, W. V. Mayneord, and (Miss) E. Roe, *J.*, 1934, 1734.

the derived hydrocarbon (XVII) to naphthalene at 280—320°.[59] L. Ruzicka and H. Waldmann point out [60] that this can be interpreted as a fission of one bond at the quaternary carbon atom and recyclisation of the four-carbon side chain at the adjacent carbon atom. Another possibility which has to be borne in mind is that of a retro-pinacolic change during the reduction of the ketone (XVI*a*) either during its direct dehydrogenation, or in the Clemmensen reduction to the hydrocarbon. Some further examples of the rearrangement of spiranes during selenium dehydrogenation are recorded by J. W. Cook and C. L. Hewett.[61]

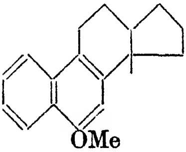
(XVI*a*.)



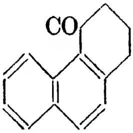


(XVII.)

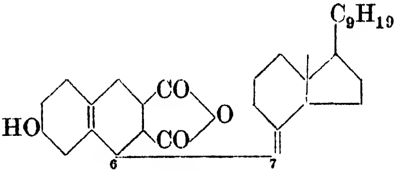
Oxygenated Compounds.—Selenium is particularly prone to eliminate oxygen-containing groups during dehydrogenation. A number of examples of the survival of an aromatic methoxyl group are on record,[62] although G. A. R. Kon and F. C. J. Ruzicka observed [63] that the methoxyl group of (XVIII) was only retained if the temperature of dehydrogenation was kept below 300°.



(XVIII.)



(XIX.)



(XX.)

The elimination of a carboxyl group, particularly when substituted on a hydroaromatic side chain, is common; [64] and angular carbethoxyl groups are also eliminated,[65] naturally enough.

There are many examples of the reduction of a cyclic keto-group during selenium dehydrogenation, for example, in the formation of phenanthrene (from the ketone XIX),[66] of benzpyrene,[66, 67] and of

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[59] *J.*, 1933, 352.

[60] *Helv. Chim. Acta*, 1933, **16**, 842.

[61] *J.*, 1934, 365.

[62] See, *e.g.*, P. Hill, W. F. Short, and (Miss) A. Higginbottom; W. F. Short, H. Stromberg, and A. E. Wiles, *J.*, 1936, 317, 319.

[63] *J.*, 1936, 187.

[64] G. Darzens and A. Lévy, *Compt. rend.*, 1934, **199**, 1131; 1935, **201**, 730; 1936, **202**, 427.

[65] J. C. Bardhan and S. C. Sengupta, *J.*, 1932, 2520, 2798; L. F. Fieser and H. L. Holmes, *J. Amer. Chem. Soc.*, 1936, **58**, 2319.

[66] J. W. Cook and C. L. Hewett, *J.*, 1933, 403.

[67] A. Winterstein and H. Vetter, *Z. physiol. Chem.*, 1934, **230**, 169.

chrysene [68] from ketonic hydro-derivatives. L. Ruzicka [69] has recently succeeded in dehydrogenating *trans*-β-decalone and 1-methyl-Δ^1-*cyclo*hexen-3-one to β-naphthol and *m*-cresol respectively at a comparatively low temperature (260°), but the yields are rather poor. At an even lower temperature (230°), C. Dorée and V. A. Petrow [70] made the interesting observation that cholesterol with selenium yields cholestanone, cholestanol and cholestenone.

Perhaps the most remarkable reaction of selenium with oxygenated compounds is that observed by A. Windaus and W. Thiele,[71] who obtained 2 : 3-dimethylnaphthalene from the dihydro-derivative of the maleic anhydride adduct of vitamin-D_2 (XX). This was interpreted as a fission of the 6 : 7-bond, followed by reduction of the anhydride ring to two methyl groups. This has been confirmed by W. Thiele and G. Trautmann's observations [72] that naphthalene-2 : 3-dicarboxylic anhydride was converted by treatment with selenium and a hydrogen donor (*p*-*cyclo*hexylphenol) at 320—325° into 2 : 3-dimethylnaphthalene. By somewhat similar treatment, one of the carboxyl groups of 1 : 8-naphthalic anhydride was reduced and one eliminated with the formation of 1-methylnaphthalene. L. Ruzicka [69] has obtained an analogous result, and has also succeeded in dehydrogenating esters of hydroaromatic acids to the corresponding free aromatic acids with loss of the ester group but no decarboxylation.

(3) *Catalytic Metals.*

The catalytic dehydrogenation of hydroaromatic substances of known structure has been fairly fully studied, but the method has not perhaps been so generally used for structural determination as has that involving the use of selenium, although there are signs that it is now beginning to come into favour. The most fully investigated catalysts are platinum, palladium, and nickel, of which the first two are the most satisfactory, as the use of nickel may lead to deposition of carbon on the catalyst, elimination of hydrocarbon fragments and other side reactions.[73] Between the two noble metals there is a general resemblance in behaviour and only minor differences in activity. Some preliminary experiments have been made on the use of rhodium and iridium.[74] Platinum and palladium catalysts for dehydrogenation are normally prepared by reduction of aqueous

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[68] D. A. Peak and R. Robinson, *J.*, 1936, 760.

[69] *Helv. Chim. Acta*, 1936, **19**, 419.

[70] *J.*, 1935, 1391.

[71] *Annalen*, 1935, **521**, 160.

[72] *Ber.*, 1935, **68**, 2245.

[73] For a recent example of this, see V. N. Ipatiev and V. I. Komarevski, *J. Amer. Chem. Soc.*, 1936, **58**, 922.

[74] N. D. Zelinski and M. B. Turova-Pollak, *Ber.*, 1925, **58**, 1298.

solutions of salts of the metals by hydrogen, formaldehyde [75] or formic acid,[76] if necessary in the presence of a carrier such as charcoal, asbestos, etc. The activity of the catalyst may depend to a considerable extent on the presence of traces of impurities, such as alkali metals, or halogen compounds. K. Packendorff and L. Leder-Packendorff [77] have made an interesting study of the selective poisoning of a catalyst for hydrogenation, while leaving the dehydrogenating properties unimpaired. The catalytic dehydrogenation of the simpler compounds is usually carried out in the vapour phase in an atmosphere of hydrogen or an inert gas, sometimes under reduced pressure. Many natural products of more complex structure have been dehydrogenated in the liquid phase.

Normal Dehydrogenation.—The use of the noble metals as dehydrogenating catalysts is largely due to N. D. Zelinski and his co-workers. Following P. Sabatier's demonstration [78] that nickel catalysed the hydrogenation of benzene at about 180°, and the dehydrogenation of *cyclo*hexane at 250—300°, Zelinski [79] observed that the dehydrogenation activity of noble metals on *cyclo*hexane and its homologues became appreciable at about 170° and was maximal at 300°, whereas rapid hydrogenation of benzene in hydrogen over the same catalyst occurred at 100°. Moreover, it was found that under dehydrogenating conditions *cyclo*pentane derivatives were unaffected, so that mixtures of the two types of alicyclic compounds could be separated by selective dehydrogenation over platinum at 300°.[80] Recent work has shown that there is a tendency for the reductive fission of *cyclo*pentane rings under these conditions, but this does not affect the general principle. Other ring systems also undergo alterations of carbon skeleton (see later), but the 6-membered ring is unique in dehydrogenating normally.

A kinetic study of the dehydrogenation of *cyclo*hexane over noble metals was made by N. D. Zelinski and N. Pavlov.[81] The method has been applied successfully to various alkyl derivatives such as hexahydroxylenes,[82] menthane,[82] and cadinene.[83] There is no evidence for the migration of alkyl groups, except in cases when a

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[75] See, *e.g.*, O. Loew, *Ber.*, 1890, **23**, 289; N. D. Zelinski and P. P. Borissov, *ibid.*, 1924, **57**, 150.

[76] See, *e.g.*, N. D. Zelinski and N. Glinka, *ibid.*, 1911, **44**, 2305; H. Wieland, *ibid.*, 1912, **45**, 486.

[77] *Ibid.*, 1934, **67**, 1388; compare K. W. Rosenmund and collaborators, *ibid.*, 1921, **54**, 425, 638, etc.

[78] For example, *ibid.*, 1911, **44**, 1984.

[79] *Ibid.*, p. 3121.

[80] N. D. Zelinski, *ibid.*, 1912, **45**, 3678.

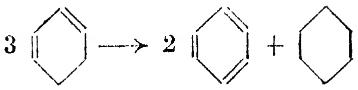
[81] *Ibid.*, 1923, **56**, 1250.

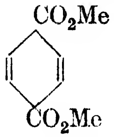
[82] N. D. Zelinski, *ibid.*, p. 787.

[83] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1924, **7**, 84.

neighbouring substituent (such as hydroxyl) is eliminated.[84] Unsaturated side chains are reduced in the usual way.[83, 85] Generally speaking, there is no difficulty in dehydrogenating fully saturated mono- or poly-cyclic compounds catalytically, unless they contain a quaternary carbon atom. Decalin gives naphthalene easily,[86, 91] and, for example, hexahydrozingiberene,[87] 2-benzyldecalin,[88] and hexahydrofluorene [88] all give their aromatic counterparts. Hexahydrohydrindene yields hydrindene.[89] The general method has been applied to the dehydrogenation of the " naphthenes " of petroleum [90] and of tar oils.[91]

Disproportionation of Hydrogen.—It has been said that fully reduced aromatic derivatives are readily dehydrogenated over noble metals; the reaction with partly reduced compounds, such as *cyclo*hexene and *cyclo*hexadienes, is more complicated. In the presence of platinum and palladium at high temperatures substances of these types rapidly undergo a disproportionation of hydrogen with the formation of a mixture of aromatic and fully saturated alicyclic compounds, thus :





(XXI.)

Reactions of this type were first observed by E. Knoevenagel and his collaborators [92, 93] in 1903. Of particular interest in the present connection is the discovery [93] that $\Delta^{2:5}$-dihydroterephthalic ester (XXI) yielded a mixture of terephthalic ester and its *cis*- and *trans*-hexahydro-derivatives when heated with palladium-black at 140° and above. Little hydrogen was evolved under these conditions. This important observation was extended by the work of N. D. Zelinski and N. Glinka,[94] and H. Wieland.[95] Wieland noticed *inter alia* that when dihydronaphthalene was treated with oxygen-

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[84] See, *e.g.*, L. Ruzicka, K. Hofmann, and J. Frei, *Helv. Chim. Acta*, 1936, **19**, 386.

[85] J. W. Cook and G. A. D. Haslewood, *J.*, 1935, 767.

[86] N. D. Zelinski, *Ber.*, 1923, **56**, 1923.

[87] L. Ruzicka and A. G. van Veen, *Annalen*, 1929, **468**, 133.

[88] J. W. Cook and C. L. Hewett, *J.*, 1936, 62.

[89] N. D. Zelinski and I. N. Titz, *Ber.*, 1929, **62**, 2869.

[90] N. D. Zelinski, *ibid.*, 1923, **56**, 1718.

[91] H. Kaffer, *ibid.*, 1924, **57**, 1261.

[92] E. Knoevenagel and W. Heckel, *ibid.*, 1903, **36**, 2816; E. Knoevenagel and J. Fuchs, *ibid.*, p. 2848; E. Knoevenagel and B. Bergdolt, *ibid.*, p. 2961.

[93] E. Knoevenagel and B. Bergdolt, *ibid.*, p. 2957.

[94] *Ibid.*, 1911, **44**, 2305, 3121.

[95] *Ibid.*, 1912, **45**, 486.

free palladium-black, it was converted into naphthalene and tetralin, with evolution of heat. J. Boëseken[96] commented upon the fact that the heats of combustion of *cyclo*hexene and *cyclo*hexadiene were appreciably lower than those of equivalent mixtures of *cyclo*hexane and benzene, and observed that *cyclo*hexene was metastable even at room temperature in presence of palladium. The disproportionation of these compounds over noble metals has been more fully studied by N. D. Zelinski and his collaborators.[97] It was observed that one passage of the vapour of *cyclo*hexene or *cyclo*hexadienes over the catalyst effected a complete conversion into *cyclo*hexane and benzene. The reaction also occurred in the liquid phase. Moreover, it was found[98] that the various methyl*cyclo*hexenes and methylene-*cyclo*hexane alike gave a mixture of methyl*cyclo*hexane and toluene. Similar results have been obtained among terpenes and related compounds. Limonene over platinum at 180° yields a mixture of *p*-cymene and menthane;[99] pinene gives pinane and (?) cymene over palladium at 190°;[1] piperitone gives menthone and thymol over nickel[2] or over palladium;[3] allyl-Δ^1-*cyclo*hexene yields *n*-propylbenzene and *n*-propyl*cyclo*hexane.[4] Many of these changes involve the hydrogenation of an extracyclic double bond, and this suggests that in general the essential reaction is the hydrogenation of double bonds by activated hydrogens from the same or surrounding molecules. In this connection it is interesting that S. Akabori and T. Suzuki[5] were able to transfer hydrogen from tetralin to various unsaturated compounds in the presence of palladium-black.

Abnormal Dehydrogenations.—Substances containing a quaternary carbon atom offer considerable resistance towards catalytic dehydrogenation, and in many cases the reaction cannot be realised. For instance N. D. Zelinski[6] was unable to dehydrogenate 1 : 1-dimethyl*cyclo*hexane : this result has recently been confirmed with a very active catalyst.[7] Moreover, G. R. Clemo and H. G. Dickenson

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[96] *Rec. trav. chim.*, 1918, **37**, 255; cf. *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 492.

[97] N. D. Zelinski and N. Pavlov, *Ber.*, 1924, **57**, 1066; 1933, **66**, 1420; N. D. Zelinski, *ibid.*, 1925, **58**, 185.

[98] N. D. Zelinski, *ibid.*, 1924, **57**, 2055.

[99] *Idem, ibid.*, p. 2058.

[1] *Idem, ibid.*, 1925, **58**, 864.

[2] W. Treibs and Harry Schmidt, *ibid.*, 1927, **60**, 2335.

[3] J. Read, A. J. Watters, G. J. Robertson, and R. S. Hughesdon, *J.*, 1929, 2068.

[4] R. J. Levina and D. M. Trachtenberg, *J. Gen. Chem. Russia*, 1936, **6**, 764.

[5] *Proc. Imp. Acad. Tokyo*, 1929, **5**, 255.

[6] *Ber.*, 1923, **56**, 1716.

[7] N. D. Zelinski, K. Packendorff, and E. G. Chocklova, *ibid.*, 1935, **68**, 98.

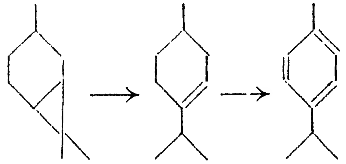
were unable to dehydrogenate 9-methyldecalin over platinum.[8] On the other hand the generalisation sometimes made, that metallic catalysts are unable to bring about dehydrogenations involving the elimination of an angular methyl group, is incorrect. L. Ruzicka and H. Waldmann [9] obtained a yield of no less than 90% of retene by dehydrogenating abietic acid (VIII) with palladised charcoal, and one of 85% from fichtelite (X).[10] The gas evolved was in each case a mixture of hydrogen and methane. Fichtelite yielded a mixture of about 8 volumes of hydrogen to 1 of methane, which represents a fair approximation to the 6 : 1 ratio required for the equation

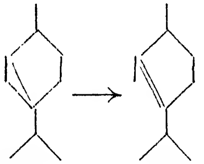
$$C_{19}H_{34} = C_{18}H_{18} + CH_4 + 6H_2$$

There is therefore strong evidence that the elimination of a tertiary methyl group can occur during catalytic dehydrogenation. The reason for the difference between the natural and the synthetic compounds is not apparent.

A similar elimination underlies O. Diels and W. Gädke's classical preparation [11] of chrysene from cholesterol and palladium, although here the reaction is complicated by a ring enlargement. L. Ruzicka and E. Peyer [12] describe an analogous rearrangement in the formation of naphthalene from α-methylhydrindene over palladised charcoal at 450°. C. D. Nenitzescu and E. Ciorănescu [13] similarly obtained a small yield of naphthalene from α-methylhydrindene and α-methylhexahydrohydrindene by passage over platinised charcoal at 310—350°.

Rings other than Six-membered.—N. D. Zelinski and R. J. Levina [14] investigated the behaviour of terpenes containing *cyclo*propane and *cyclo*butane rings towards dehydrogenating catalysts. It was found that such rings were opened with the formation of an unsaturated isomeride, the subsequent behaviour of which depended upon the structure. Thus carane (XXII) yielded *p*-cymene by the above route


(XXII.)


(XXIII.) (XXIV.)

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[8] *J.*, 1935, 735; for another negative example see J. W. Cook, G. A. D. Haslewood, and (Mrs.) A. M. Robinson, *J.*, 1936, 667.

[9] *Helv. Chim. Acta*, 1933, **16**, 842.

[10] *Idem*, *ibid.*, 1935, **18**, 611.

[11] *Ber.*, 1925, **58**, 1231; 1927, **60**, 140.

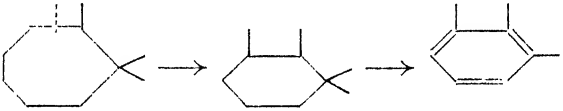
[12] *Helv. Chim. Acta*, 1935, **18**, 676.

[13] *Ber.*, 1936, **69**, 1040.

[14] *Annalen*, 1929, **476**, 60.

whereas thujane (XXIII) isomerised to a *cyclo*pentene derivative (such as XXIV) which resisted dehydrogenation. Pinane yielded some *p*-cymene by a process involving fission of the *cyclo*butane ring, but compounds containing five-membered rings were stable and suffered neither dehydrogenation nor disproportionation. A few experiments have been carried out with rings larger than six-membered.[15] L. Ruzicka and C. F. Seidel [16] found that 1 : 1 : 2-trimethyl*cyclo*heptane (XXV), with palladised charcoal at 420°, yielded a hydrocarbon oxidising to hemimellitic acid and hence having the structure (XXVI).

(XXV.)



(XXVI.)

N. D. Zelinski and M. G. Friemann [17] observed that *cyclo*octane, after passing over a platinum catalyst at 300°, suffered a fall in boiling point, density and refractivity, but the product was not identified.

The behaviour of the *cyclo*pentane ring is, in contrast, well established. As has already been mentioned, the early work of Zelinski showed that simple *cyclo*pentane compounds were unaffected by metallic catalysts. Apparent exceptions were found [18] in " *cyclo*hexyl-*cyclo*pentane " and " *cyclo*hexyl-methyl*cyclo*pentane " which yielded diphenyl. The alicyclic hydrocarbons were made by reducing, with zinc and hydriodic and acetic acids, the carbinols obtained from *cyclo*hexylmagnesium bromide and *cyclo*pentanone or methyl*cyclo*pentanone. Reinvestigation showed that the diphenyl originated in di*cyclo*hexyl formed during the preparation of the Grignard compound.[19] The need for caution in the choice of synthetic methods is also illustrated in investigations of the dehydrogenation of di*cyclo*pentyl [20] (XXVII). When this was made by the Würtz reaction from *cyclo*pentyl bromide, it resisted dehydrogenation, but material made by reducing the pinacol from *cyclo*pentanone (XXVIII) gave naphthalene on treatment with platinised charcoal. It was deduced that only the first material was authentic and that re-

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[15] See in particular A. St. Pfau and P. Plattner's important investigations on the formation of azulenes from derivatives of 0 : 3 : 5-*bicyclo*decane (*Helv. Chim. Acta*, 1936, **19**, 858). Considerations of space prevent a full discussion of these interesting substances in this Report.

[16] *Helv. Chim. Acta*, 1936, **19**, 424.

[17] *Ber.*, 1930, **63**, 1485.

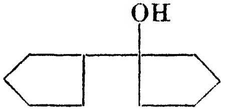
[18] N. D. Zelinski, *ibid.*, 1925, **58**, 2755.

[19] N. D. Zelinski and I. N. Titz, *ibid.*, 1931, **64**, 183.

[20] N. D. Zelinski, I. N. Titz, and L. Fatajev, *ibid.*, 1926, **59**, 2580.

arrangement to decalins must have accompanied the reduction of the pinacol.

(XXVII.)



(XXVIII.)

A number of other examples of the inertia of *cyclo*pentane rings towards dehydrogenation have recently been recorded.[19, 20a] J. W. Barrett and R. P. Linstead [21] find that *cis*-0 : 3 : 3-*bicyclo*-octane (formed by *ortho*-fusion of two such rings) is stable to platinum at 310°. N. D. Zelinski, B. A. Kazanski, and A. F. Plate [22] have, however, observed that *cyclo*pentane is *hydrogenated* in an atmosphere of hydrogen at 300° over platinised charcoal to yield *n*-pentane, and other examples of the hydrogenation of the five-membered ring have since come to light.[23] This extension of the series commenced by the comparatively easily reducible three- and four-membered rings is of considerable interest. A further complication is introduced by the recent work of B. A. Kazanski and A. F. Plate,[24] who announce that *n*-butyl*cyclo*pentane and similar hydrocarbons on passage over platinised charcoal in hydrogen or an inert gas at 300—310° yield a mixture of aromatic and aliphatic hydrocarbons. The aromatic hydrocarbons could be formed either by cyclisation of the side chain and fission of the five-membered ring, or by the formation and subsequent cyclisation of aliphatic hydrocarbons. In support of the second hypothesis, they find that aromatic hydrocarbons can be formed by the cyclo-dehydrogenation of various aliphatic hydrocarbons, for example, *p*-xylene from di*iso*butyl and *m*-cymene from di*iso*amyl. The yields of aromatic substances in this work are, however, low.

The formation of new rings under the conditions of catalytic dehydrogenation is not a new phenomenon, although no such striking results as the above have previously been obtained. N. D. Zelinski, I. N. Titz, and M. V. Gaverdowskaja [25] observed the formation of fluorene from diphenyl- or di*cyclo*hexyl-methane and of phenanthrene from αβ-diphenylethane over platinised charcoal at 300° and analogous cyclo-dehydrogenations of alcohols have been achieved.[26]

[20a] N. D. Zelinski, S. E. Michlina, and M. S. Eventova, *Ber.*, 1933, **66**, 1422.

[21] *J.*, 1936, 611.

[22] *Ber.*, 1933, **66**, 1415.

[23] N. D. Zelinski and B. A. Kazanski, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 168; J. I. Denissenko, *Ber.*, 1936, **69**, 1353.

[24] *Ibid.*, p. 1862.

[25] *Ibid.*, 1926, **59**, 2590.

[26] N. D. Zelinski and M. V. Gaverdowskaja, *ibid.*, 1928, **61**, 1049.

From further work,[27] N. D. Zelinski and I. N. Titz have come to the general conclusion that six-membered rings can be involved in the formation of new rings by dehydrogenation, but the same is not true of *cyclo*pentane rings.

Oxygenated Compounds.—Although there is naturally a decided tendency for the reduction of ketonic and alcoholic groups during catalytic dehydrogenation, there are a number of examples in which the oxygen is preserved with the formation of a phenol. Of these we may mention H. Honigmann's preparation of dehydroneoergosterol from neoergosterol (Pt at 270°);[28] L. Ruzicka and E. Mörgeli's dehydrogenation of 7-methyl-1-tetralone to 7-methyl-1-naphthol, in 60% yield (Pd at 310°)[29]; and J. W. Cook, C. L. Hewett, and C. A. Lawrence's conversion of octahydro-9-phenanthrol into 9-phenanthrol (Pt at 300°).[30] Methoxyl groups on aromatic rings survive catalytic dehydrogenation.[31] Angular carboxyl groups are eliminated.[32]

General.—The above is a largely empirical review of the main facts. Comparatively little is known with certainty of the mechanisms of the various processes, and it would be premature to discuss this at any length. The catalytic and "chemical" processes must be essentially different. It is probable that the fundamental stages in catalytic dehydrogenation are (i) activation of hydrogen by the metal, followed by (ii*a*) elimination of this hydrogen as such, or (ii*b*) its addition to an unsaturated centre (but not to an aromatic centre) in the same or a neighbouring molecule. On the other hand, dehydrogenation by means of sulphur or selenium presumably involves (i) an addition of the reagent to an unsaturated or aromatic centre, followed by (ii) an elimination of hydrogen sulphide or selenide. Such a difference in mechanism would account *inter alia* for the fact that saturated hydroaromatic compounds are dehydrogenated readily over catalysts, but not by sulphur or selenium under normal conditions.

R. P. L.

6. SYNTHESIS OF POLYCYCLIC HYDROAROMATIC COMPOUNDS.

The sudden concentration of research in a large number of centres on this field has been one of the features of organic chemistry during

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[27] *Ber.*, 1929, **62**, 2869; 1931, **64**, 183.

[28] *Annalen*, 1934, **511**, 292.

[29] *Helv. Chim. Acta*, 1936, **19**, 377.

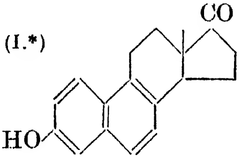
[30] *J.*, 1936, 71.

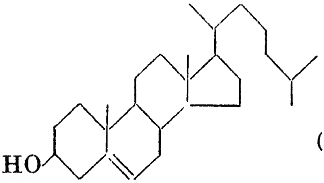
[31] See, *e.g.*, L. Ruzicka, H. Hösli, and K. Hofmann, *Helv. Chim. Acta*, 1936, **19**, 370.

[32] See, *e.g.*, L. Ruzicka, L. Ehmann, M. W. Goldberg, and H. Hösli, *ibid.*, 1933, **16**, 833.

the past four years. The driving force has of course been the discovery that a large and important class of natural products contains condensed alicyclic structures. The synthesis of some of the natural products themselves is a distinct possibility and provides a clear objective, for example, that of the hormone equilenin (I). In other molecules, *e.g.*, cholesterol (II), the stereochemical complications are such that the prospect of a total synthesis is more remote. But besides the synthesis of actual natural products with a view to confirmation of structure, much work is necessary on the reactions, stereochemical relationships, and biological activity of compounds of the general type. For this purpose synthetic compounds of known structure are required.

(I.*)





(II.*)

Progress in the chemistry of the natural products themselves is dealt with in another section of these Reports. The present review is concerned with a correlation of the synthetic work. It would be possible to systematise this in several ways : (*a*) In terms of the type of ring structure synthesised, *e.g.*, hydrophenanthrene; (*b*) in terms of the natural product aimed at, *e.g.*, equilenin; (*c*) in terms of physiological activity, *e.g.*, oestrogenic or carcinogenic compounds. A more fundamental chemical division is that based on the methods actually involved in the formation of the polycyclic

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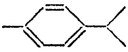
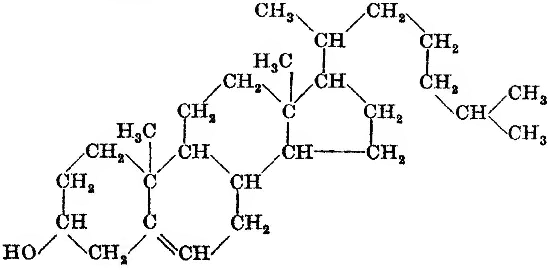
* *General note on formulæ.* For the sake of clarity, the following convention is adopted throughout this section of the Report. Aromatic rings are written in Kekulé forms with the double bonds in full, and simple hexagons denote *cyclo*hexane rings. Side chains are represented by straight lines, each corner representing a carbon atom, and a single straight line a methyl group. Thus *p*-cymene becomes  and the formula (II) above represents the full molecule :



structure. This is adopted in the present Report, the methods being divided as follows : *

(1) Reduction of aromatic rings.

(2) Cyclisation involving two double bonds in the same molecule; cyclo-dehydration of unsaturated alcohols.

(3) Cyclisation involving a double bond and an aromatic nucleus; cyclo-dehydration of aromatic alcohols.

(4) Cyclisation involving double bonds in different molecules (diene synthesis).

(5) Cyclo-dehydration of ketonic esters and diketones.

(6) Formation of cyclic ketones from monocarboxylic acids and their derivatives.

(7) Formation of cyclic ketones from dibasic acids.

(1) *Reduction of Aromatic Rings.*

This, logically the first method of approach, is of little practical value and cannot, of course, be applied to the synthesis of substances containing an angular methyl group. Its principal drawback lies in the difficulty of separating the reduction products and in the stereochemical complications. The course of the hydrogenation of naphthalene and its simple derivatives is now clear, thanks mainly to the work of G. Schroeter [1] and W. Hückel.[2] The pressure hydrogenation of phenanthrene in the liquid phase over nickel has been investigated by Schroeter,[3] who finds that normally the symmetrical octahydro-derivative (V) is formed but that under suitable conditions the 1 : 2 : 3 : 4-tetrahydro- (IV) and 9 : 10-dihydro- (III) compounds [4] can be isolated.

Separation of these is possible because (IV), which alone possesses an intact naphthalene group, is the only reduction product capable of forming a picrate, whilst (V) yields an insoluble monosulphonic acid and (III) a soluble disulphonic acid. These three compounds are crystalline solids; many of the oily hydrophenanthrenes of the literature [5] must be impure. The structures of (IV) and (V) have been confirmed by their oxidation by chromic acid to monoketones (mainly 1-keto- from V, and, curiously enough, 4-keto- from IV)

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[1] *Annalen*, 1922, **426**, 1.

[2] *Ann. Reports*, 1935, **32**, 307.

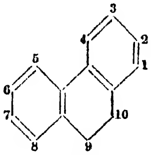
[3] *Ber.*, 1924, **57**, 2025.

[4] G. Schroeter, H. Müller, and J. V. S. Huang, *Ber.*, 1929, **62**, 645.

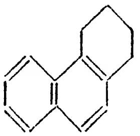
[5] Reviewed by Schroeter, ref. 3.

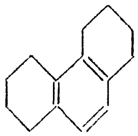
* The period under review is essentially 1933—1936, but some earlier work is included to make a connected account. Only partly or fully reduced aromatic substances are dealt with, purely aromatic syntheses not being considered. A correlation between the reduced compounds and their aromatic analogues will be found in the section on Dehydrogenation (p. 294).

which have been independently synthesised.[3, 4] The structure of (III) has been proved by synthesis.[4] The optical properties of (V) are in agreement with the location of the eight hydrogen atoms on the outside rings.[6] More recently it has been found that hydrogenation of phenanthrene over the mixed oxides of copper, chromium and barium yields the 9 : 10-dihydro-compound (III),[7] whilst the use of Raney nickel leads to the *s*.-octahydro-derivative,[8] in good yields. A complete hydrogenation to perhydrophenanthrenes over Raney nickel under vigorous conditions has also been reported.[9] The hydrogenation of anthracene has also been studied by G. Schroeter, whose results [10] differ in many respects from earlier work.[11] It is instructive that in the presence of hydrogen-activating catalysts the only partial reduction products which appear capable of isolation are those containing one or more intact aromatic rings and no superfluous double bonds.



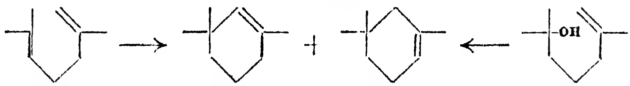
(III.)


(IV.)


(V.)

(2) *Cyclisation involving Two Double Bonds in the Same Molecule ; Cyclo-dehydration of Unsaturated Alcohols.*

Cyclisations of this class are fairly common in the early literature of terpene chemistry. The first recorded was that of geraniolene (VI) into a mixture of α- and β-*cyclo*geraniolenes (VIII and VII) by the action of sulphuric acid,[12] and a number of similar reactions were soon discovered.[13] This is a typical cyclisation of a diolefin;



(VI.) (VII.) (VIII.) (IX.)

[6] K. von Auwers and F. Krollpfeiffer, *Annalen*, 1922, **430**, 253.

[7] A. Burger and E. Mosettig, *J. Amer. Chem. Soc.*, 1935, **57**, 2731.

[8] J. van de Kamp and E. Mosettig, *ibid.*, p. 1107.

[9] P. S. Pinkney, G. A. Nesty, R. H. Wiley, and C. S. Marvel, *ibid.*, 1936, **58**, 972.

[10] *Ber.*, 1924, **57**, 2003.

[11] Godchot, *Bull. Soc. chim.*, 1907, [iv], **1**, 121, 701.

[12] F. Tiemann and F. W. Semmler, *Ber.*, 1893, **26**, 2727; F. Tiemann *Ber.*, 1900; **33**, 3711; O. Wallach and M. Franke, *Annalen*, 1902, **324**, 101.

[13] *E.g.*, F. W. Semmler, *Ber.*, 1894, **27**, 2520.

closely allied is the cyclo-dehydration of olefinic alcohols, for example, the conversion of the dimethylheptenol (IX) into α-*cyclo*geraniolene (VIII) by phosphoric acid.[14] The mechanism of these reactions need not be discussed; it is sufficient to note that under the conditions of reaction the diene and unsaturated alcohol are more or less equivalent. Cyclisation between two double bonds has been observed among compounds containing the aldehyde,[15] ketone,[16] and acid [17] groups. The well-known cyclisations of linalool and geraniol to terpineol and allied compounds also belong to this type. Whether a cyclic alcohol or a mono-olefinic cyclic hydrocarbon is the actual product is determined by the structure and the conditions of the reaction. The addition of the elements of water (or acetic acid, etc.) may follow the actual cyclisation.

The structural conditions necessary for the cyclo-dehydration of olefinic alcohols have recently been investigated by D. C. Hibbit and R. P. Linstead.[18] It was found that the methylheptenol (X), containing a terminal double bond, readily yielded the corresponding dimethyl*cyclo*hexene (XI), but when the double bond was nearer the alcohol group no cyclisation occurred. The formation of *cyclo*pentene rings was not observed.

(X.)


(XI.)

The first direct synthesis of dicyclic compounds from the corresponding olefins was that of L. Ruzicka and E. Capato.[19] It had previously been observed [20] that dehydration of farnesol (XII) with potassium hydrogen sulphate yielded the aliphatic sesquiterpene farnesene (XIII), which with hot formic acid yielded a cyclic isomeride. It was then found that the easily synthesised [20] nerolidol (XIV) was dehydrated by acetic anhydride to an acyclic hydrocarbon (probably farnesene), which yielded the monocyclic α-bisabolol (XV) on treatment with acetic and sulphuric acids. When, however, nerolidol was boiled with formic acid, a double cyclisation occurred with the formation of a hydrocarbon con-

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[14] C. D. Harries and R. Weil, *Ber.*, 1904, **37**, 848; compare C. D. Harries, *Annalen*, 1905, **343**, 362.

[15] F. Tiemann, *Ber.*, 1900, **33**, 3719.

[16] F. Tiemann and P. Krüger, *ibid.*, 1893, **26**, 2675.

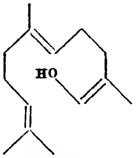
[17] F. Tiemann and F. W. Semmler, *ibid.*, p. 2725.

[18] *J.*, 1936, 470.

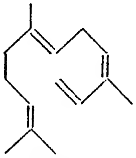
[19] *Helv. Chim. Acta*, 1925, **8**, 259.

[20] L. Ruzicka, *ibid.*, 1923, **6**, 490. Other early examples of the same reaction are the formation of polycyclic hydrocarbons from α-camphorene (L. Ruzicka, *ibid.*, 1924, **7**, 279) and from squalene (I. M. Heilbron, E. O. Kamm, and W. M. Owens, *J.*, 1926, 1630).

taining hexahydrocadalene (XVI, position of double bonds unknown). The presence of the naphthalene skeleton was shown by the dehydrogenation of (XVI) to cadalene.



(XII.)



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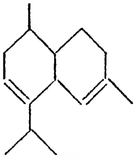
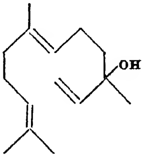
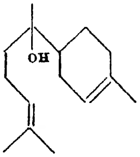


(XVI.)

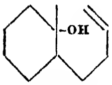
(XIV.)



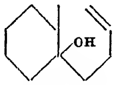


(XV.)

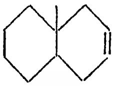
Simpler examples of the formation of a hydronaphthalene have recently been realised by D. C. Hibbit, R. P. Linstead, and A. F. Millidge [21, 18, 22] in the cyclisation of 1-methyl-2-Δ^{γ}-butenyl-*cyclo*hexanol (XVII) and its isomeride (XVIII) to 9-methyl-Δ^{2}-octalin (XIX). The cyclising reagents were phosphoric acid and its anhydride. The formation of the dicyclic hydrocarbon was proved by its degradation through 8-methylhydrindanone to 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid (XX), which was



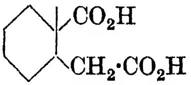
(XVII.)



(XVIII.)



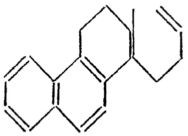
(XIX.)

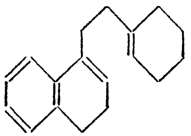


(XX.)

independently synthesised.[23] The cyclisation of a compound containing a Δ^{γ}-butenyl side chain was independently examined by A. Cohen, J. W. Cook, and C. L. Hewett,[24] who found that

(XXI.)





(XXII.)

2-methyl-1-Δ^{γ}-butenyl-3 : 4-dihydrophenanthrene (XXI) yielded a tetracyclic isomeride with sulphuric–acetic acids, which could be dehydrogenated to chrysene. The cyclisation of the tricyclic diene

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[21] R. P. Linstead, *Chem. and Ind.*, 1935, **54**, 315.

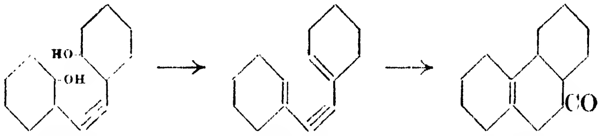
[22] D. C. Hibbit, R. P. Linstead, and A. F. Millidge, *J.*, 1936, 476.

[23] R. P. Linstead and A. F. Millidge, *ibid.*, p. 478.

[24] *J.*, 1935, 1633; J. W. Cook, *Chem. and Ind.*, 1935, **54**, 315.

(XXII) to a hydrochrysene has also been achieved,[25] but is complicated by resinification.

An interesting extension of the method is to hydrocarbons containing two double bonds and one triple bond. In an extension of previous work,[26] it is reported[9] that the compound (XXIV), obtained by dehydrating the acetylenic glycol (XXIII), yields a ketododecahydrophenanthrene (XXV) on treatment with formic acid or acetic–sulphuric acids. The hydrocarbons obtained by the reduction of (XXV) resembled known hydrophenanthrenes in physical properties, but the structures have not yet been confirmed by dehydrogenation.



(XXIII.) (XXIV.) (XXV.)

To summarise : Only six-membered rings can be formed by this method. It can be applied to the synthesis of compounds containing an angular methyl group. The exact structural requirements are not fully known, but in general two double bonds at the ends of a chain of six carbon atoms, or two equivalent groups, appear to be necessary.

(3) *Cyclisation involving a Double Bond and an Aromatic Nucleus ; Cyclo-dehydration of Aromatic Alcohols.*

This is a widely used method for the formation of partly reduced polycyclic aromatic compounds. It differs from the method (2), just discussed, in that one of the unsaturated centres is replaced by an aromatic nucleus. Typical cyclisations, involving an olefin and an alcohol respectively, are the formation of tetralin (XXVI) and 1-methyltetralin (XXVII) observed by M. T. Bogert, D. Davidson, and their collaborators : [27]

(XXVI.) (XXVII.)

The use of an aromatic fragment limits the value of the method for the actual synthesis of natural products, for example, of those

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[25] J. W. Cook and A. Dansi, *J.*, 1935, 500.

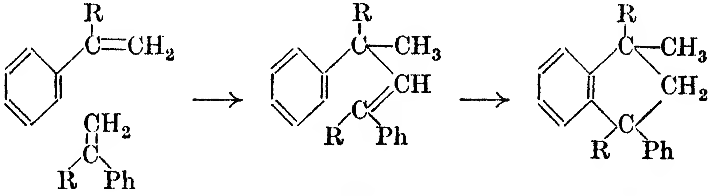
[26] A. T. Blomquist and C. S. Marvel, *J. Amer. Chem. Soc.*, 1933, **55**, 1655; D. T. Mitchell and C. S. Marvel, *ibid.*, p. 4276.

[27] Summarised in *J. Amer. Chem. Soc.*, 1935, **57**, 151.

containing an angular methyl group. On the other hand, the intermediates are generally more accessible than those of method (2) and the cyclisations proceed more readily. The process has found particular application in the synthesis of the dehydrogenation products of naturally occurring substances.

The first recorded cyclisation of this type seems to be that of benzylmenthol into methyl*iso*propylhexahydrofluorene by O. Wallach,[28] and the formation of phenylindenes from various open-chain derivatives has also been known for some time.[29] The first general synthetic work was that of G. Darzens.[29a] His experiments, however, were concerned with unsaturated acids and lactones, and it will be convenient to consider first the cyclisation of unsaturated hydrocarbons and the corresponding alcohols.

The ease of conversion of phenyl olefins into dicyclic hydrocarbons is reflected in E. Bergmann's investigations [30] of the polymerides of *as*-diphenylethylene and α-methylstyrene. It was known that both these hydrocarbons formed unsaturated liquid dimerides and saturated solid dimerides. Bergmann identified the former as substituted diphenylpropylenes (XXVIII) and the latter as the isomeric derivatives of indane (XXIX). The ring closures were brought about by stannic or aluminium chloride.



(XXVIII.) (XXIX.)

The cyclisation of aryl olefins and the corresponding alcohols has recently been widely utilised by a number of workers for the synthesis of hydrophenanthrenes and more complex structures. In an important paper in 1932 J. C. Bardhan and S.C. Sengupta [31] first described the conversion of a derivative of β-phenylethyl*cyclo*hexane into a hydrophenanthrene. The formation of dicyclic compounds

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[28] *Ber.*, 1896, **29**, 2962; *Annalen*, 1899, **305**, 261.

[29] D. Vorländer and C. Siebert, *Ber.*, 1906, **39**, 1030; E. P. Kohler, *Amer. Chem. J.*, 1908, **40**, 217; A. Orékhov and M. Tiffeneau, *Bull. Soc. chim.* 1922, [iv], **31**, 253; cf. (Mrs.) O. Blum-Bergmann, *J.*, 1935, 1020.

[29a] *Compt. rend.*, 1926, **183**, 748, and subsequent papers.

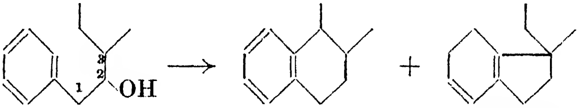
[30] E. Bergmann and H. Weiss, *Annalen*, 1930, **480**, 49; E. Bergmann, H. Taubadel, and H. Weiss, *Ber.*, 1931, **64**, 1493; compare W. Schlenk and E. Bergmann, *Annalen*, 1930, **479**, 65.

[31] *J.*, 1932, 2520.

(tetralin and indanes) from phenyl olefins followed a few years later. It will, however, be convenient to deal with this first.

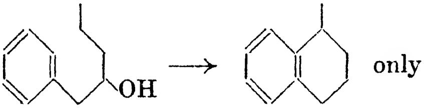
This section of the subject has been thoroughly investigated by Bogert, Davidson, and their collaborators,[32] who have studied the conversion of a large number of phenylbutanols, phenylpentanols, olefins of associated structure, and similar compounds, into the corresponding tetralins and/or indanes. Their main results can be summarised as follows : Benzene derivatives with an unbranched side chain of five to seven carbon atoms, containing a double bond or hydroxyl group, will give a tetralin on treatment with sulphuric acid except when the hydroxyl group or double bond adjoins the phenyl group, in which case polymerisation occurs. Larger rings than six-membered are not formed. When the side chain carries a methyl group on C_3 (phenyl on C_1), derivatives of both indane and tetralin are formed.

Thus :



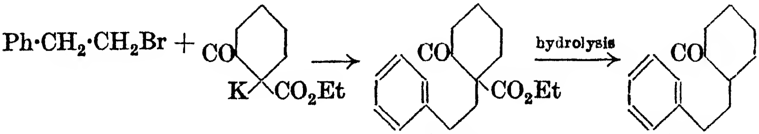
(XXIXa.)

But :



As regards mechanism, it is concluded that unsaturated hydrocarbons generally, but not invariably, intervene as intermediates. It is noteworthy that five-membered rings can be formed from these aromatic intermediates, which has not so far been found possible [18] from the non-aromatic compounds considered under method (2). This indicates the greater reactivity of hydrogen substituted in the aromatic ring.

Bardhan and Sengupta's synthesis [31] of hydrophenanthrenes proceeds in a typical case as follows :



(XXX.) (XXXI.)

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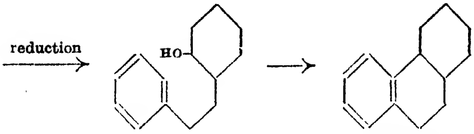
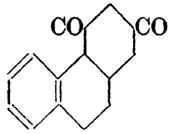
[32] M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, 1934, **56**, 185; M. T. Bogert, D. Davidson, and R. O. Roblin, *ibid.*, p. 248; M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *ibid.*, p. 959; R. O. Roblin, D. Davidson, and M. T. Bogert, *ibid.*, 1935, **57**, 151.



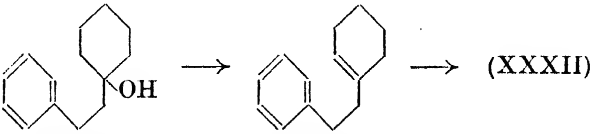
(XXXII.)



(XXXIII.)

The cyclo-dehydration was carried out by the use of phosphoric oxide at 140°. The structure of the product (XXXII) was shown by dehydrogenation to phenanthrene and by its independent preparation by the reduction of P. Rabe's[33] diketo-octahydrophenanthrene (XXXIII). The method was applied to the synthesis of various alkyl hydrophenanthrenes, and thence alkyl phenanthrenes, including retene.[34] The ketonic fission of keto-esters such as (XXX) is often difficult or impossible. In such cases, the keto-ester itself can be reduced and the hydroxy-ester cyclised to give a hydrophenanthrene containing an angular carbethoxyl group. This group is eliminated in dehydrogenation. Another method[35] of obviating this difficulty is to hydrolyse the keto-ester to the corresponding pimelic acid and recyclise.

A similar and rather simpler synthetic method was reported independently and practically simultaneously by M. T. Bogert[36] in America and J. W. Cook[37] in London, and has been widely applied by Cook and his collaborators. Bogert found that 1-β-phenylethyl*cyclo*hexanol (XXXIV), isomeric with Bardhan and Sengupta's alcohol, and easily prepared from β-phenylethylmagnesium bromide and *cyclo*hexanone, could be dehydrated by mild reagents to the olefin (XXXV), but this with concentrated sulphuric acid yielded *as.*-octahydrophenanthrene (XXXII). Experimental details of this and similar syntheses have recently appeared.[37a] To bring about the same changes J. W. Cook and C. L. Hewett[38] employed



(XXXIV.) (XXXV.)

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[33] *Ber.*, 1898, **31**, 1896.

[34] J. C. Bardhan and S. C. Sengupta, *J.*, 1932, 2798.

[35] G. A. R. Kon, *J.*, 1933, 1081.

[36] *Science*, 1933, **77**, 289.

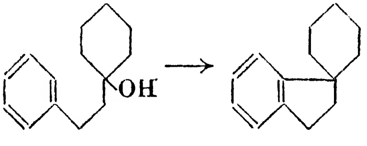
[37] *Chem. and Ind.*, 1933, 451.

[37a] D. Perlman, D. Davidson, and M. T. Bogert, *J. Org. Chem.*, 1936, **1**, 288.

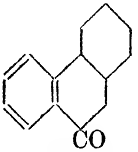
[38] *J.*, 1933, 1098.

a number of reagents, the most usual cyclising agent (XXXV ⟶ XXXII) being aluminium chloride in carbon disulphide. The tricyclic product yielded phenanthrene on dehydrogenation.

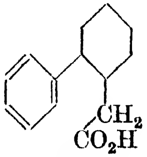
as.-Octahydrophenanthrene (XXXII) can exist in two racemic forms (*cis-* and *trans-*). The separation of two compounds, believed to be these stereoisomerides, by fractional distillation of the cyclodehydration product of 1-β-phenylethyl*cyclo*hexanol (XXXIV) has recently been reported.[39] Bogert [40, 37a] has, however, advanced convincing evidence that the lower-boiling isomeride is actually the spiran (XXXVI), the higher-boiling being the octahydrophenanthrene (XXXII). The formation of this spiran is precisely analogous to that of the indane (XXIX*a*), mentioned on p. 320. The structure of this octahydrophenanthrene has been confirmed by its oxidation [41] by means of chromic acid to the ketone (XXXVII), which was independently synthesised from 2-phenyl*cyclo*hexylacetic acid (XXXVIII). The ketone obtained in this oxidation was contaminated with an isomeric product, probably derived from the spiran (XXXVI).



(XXXVI.)

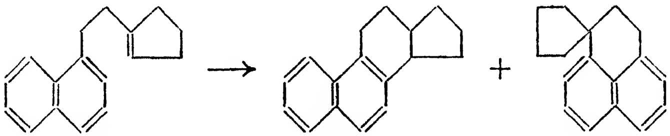


(XXXVII.)



(XXXVIII.)

The new method was applied by J. W. Cook and C. L. Hewett [38, 42] to the preparation of tetracyclic compounds. Here again it was found that the cyclisation product was a mixture of the desired hydrophenanthrene derivative and a spiran. Thus β-1-naphthylethyl*cyclo*pentene (XXXIX) on treatment with aluminium chloride yielded *cyclo*pentanotetrahydrophenanthrene (XL), containing the ætiocholane skeleton, and a *spiro*-hydrocarbon, apparently (XLI). On dehydrogenation these yielded *cyclo*pentenophenanthrene and 1-methylpyrene respectively. Similar results were obtained [42] from



(XXXIX.) (XL.) (XLI.)

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[39] J. van de Kamp and E. Mosettig, *J. Amer. Chem. Soc.*, 1936, **58**, 1063.

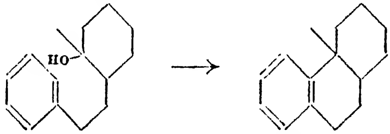
[40] M. T. Bogert, *Science*, 1936, **84**, 44.

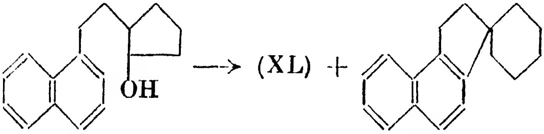
[41] J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J.*, 1936, 71.

[42] *J.*, 1934, 365.

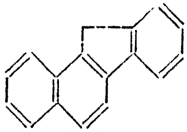
the related *cyclo*hexene derivatives, and the method was further extended to the preparation of a hydrogenated 1 : 2-benzanthracene from 2-β-phenylethyl-*trans*-octalin.

An application of the Bardhan–Sengupta method in these fields was made at the same time by G. A. R. Kon.[35] It was found that the reaction could be applied to the preparation of substances containing an angular methyl group; for example, 1-methyl-2-β-phenylethyl*cyclo*hexanol (XLII) was dehydrated to the corresponding hydrophenanthrene (XLIII), which on dehydrogenation yielded phenanthrene. Spiran formation complicates this method also. Thus, dehydration of the alcohol (XLIV) led to *cyclo*pentanotetrahydrophenanthrene (XL) and the spiran (XLV). (XL) gives *cyclo*pentenophenanthrene on dehydrogenation,[38] whilst the *spiro*-hydrocarbon yields chrysofluorene [42] (XLVI).

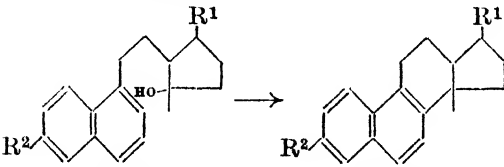
(XLII.)  (XLIII.)



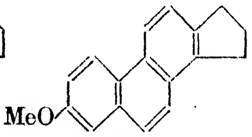
(XLIV.) (XLV.)


(XLVI.)

In subsequent experiments,[43] Kon and his collaborators applied the Bogert–Cook method to the synthesis of numerous tetracyclic hydrocarbons. These included the important $C_{18}H_{16}$ hydrocarbon of O. Diels,[44] which was also prepared by a different method by E. Bergmann and H. Hillemann.[45] The side reactions were prevented by the introduction of *o*-methyl groups into the *cyclo*pentane ring, cyclisation on to the methylated carbon proceeding to the exclusion of spiran formation.[43] Thus :



(XLVII.) (XLVIII.)



(XLIX.)

(R^2 = H, R^1 = H or Me)

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[43] S. H. Harper, G. A. R. Kon, and F. C. J. Ruzicka, *J.*, 1934, 124; D. J. C. Gamble and G. A. R. Kon, *J.*, 1935, 443; D. J. C. Gamble, G. A. R. Kon, and B. Saunders, *ibid.*, p. 644.

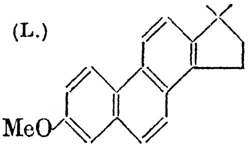
[44] *Ann. Reports*, 1933, **30**, 214.

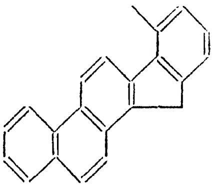
[45] *Ber.*, 1933, **66**, 1302.

This was also observed by A. Cohen, J. W. Cook, C. L. Hewett, and A. Girard[46] in their synthesis of the important 7-methoxy-1 : 2-*cyclo*pentenophenanthrene (XLIX), the dehydrogenation product of methoxyoestratriene. In this case the cyclisation (XLVII ⟶ XLVIII; $R^1 = H$, $R^2 = OMe$) by aluminium chloride went exceedingly well; the synthesis was completed by dehydrogenation of (XLVIII).

Essentially the same synthetic method has been used for the synthesis of other dehydrogenation products related to bile acids and hormones; for example, (L) derived from oestrone,[47] and L. Ruzicka's $C_{21}H_{16}$ hydrocarbon from cholic acid[48] (LI). These syntheses involved dehydrogenation of the hydroaromatic compounds as the last stage. A number of pentacyclic hydrocarbons related in structure to (LI) have also been prepared similarly, in efforts, as yet unsuccessful, to synthesise the compound $C_{25}H_{24}$ obtained by O. Diels from cholesterol.[49]

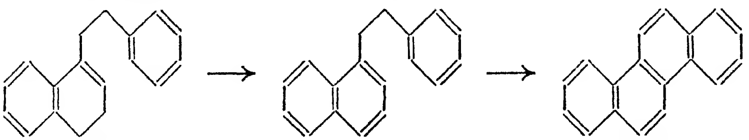
(L.)





(LI.)

An interesting variant of this reaction was discovered by L. Ruzicka and H. Hösli[50] in experiments on the cyclisation of the olefin (LII) derived from β-phenylethylmagnesium bromide and α-tetralone. When this was boiled with aluminium chloride in carbon disulphide, it evolved hydrogen chloride and yielded chrysene (LIII) directly. This involves an effective loss of six atoms of hydrogen. Picene was synthesised similarly. As dibenzyl was found to yield phenanthrene under the same conditions, and dinaphthylethane to yield picene, it appears probable that the formation of chrysene and picene by cyclo-dehydrogenations involves the intermediate formation of phenylnaphthylethane and dinaphthylethane respectively,[51] thus :



(LII.) (LIII.)

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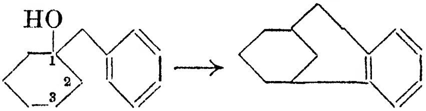
[46] *J.*, 1934, 653.

[47] A. Cohen, J. W. Cook, and C. L. Hewett, *J.*, 1935, 445.

[48] W. E. Bachmann, J. W. Cook, C. L. Hewett, and J. Iball, *J.*, 1936, 54.

The structures of the aromatic dehydrogenation products of the compounds obtained in these syntheses are in most cases certain. From these and from the method of synthesis it is possible to arrive at the probable composition of the main constituents of the hydroaromatic material. In only a few cases, however, have these been proved independently. The investigation of *as.*-octahydrophenanthrene indicates the need for caution in this field, and this is also evident from J. W. Cook and C. L. Hewett's study of the dehydration of 1-benzyl*cyclo*hexanol. It had been found [38] that treatment of this with phosphoric oxide at 160° yielded a saturated and hence tricyclic hydrocarbon. This was thought to be a hexahydrofluorene, although it could not be dehydrogenated to fluorene. Later work,[52] however, showed that authentic hexahydrofluorene readily yielded fluorene on treatment with selenium or platinum, and the tricyclic hydrocarbon was found to be benz-1 : 3 : 3-*bicyclo*-Δ^2-nonene (LIV). The *cyclo*hexane ring had become fused to benzene by the 3- and not the 2-carbon atom.



(LIV.)

Another possible complication in such syntheses lies in a molecular rearrangement of the carbon skeleton.* Thus the condensation of β-phenylethylmagnesium bromide and *cyclo*hexene oxide was first thought to yield 2-β-phenylethyl*cyclo*hexanol, and the chloride of this with aluminium chloride was thought to give *as.*-octahydrophenanthrene.[52a] Later investigation showed that the original alcoholic product was actually β-phenylethyl*cyclo*pentylcarbinol.[41, 52b] Complete failures to cyclise by the method are rare, but 1-1′-naphthyl-Δ^1-*cyclo*hexene was quite unchanged by the action of aluminium chloride in cold carbon disulphide, although a methyl derivative gave evidence of a little cyclisation.[53]

Compounds containing Negative Groups.—It is convenient to con-

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[49] J. W. Cook, C. L. Hewett, W. V. Mayneord, and (Miss) E. Roe, *J.*, 1934, 1727.

[50] *Helv. Chim. Acta*, 1934, **17**, 470.

[51] Compare J. W. Cook and C. L. Hewett, *J.*, 1934, 369.

[52] J. W. Cook and C. L. Hewett, *J.*, 1936, 62.

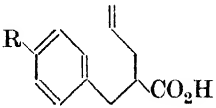
[52a] J. D. Fulton and R. Robinson, *J.*, 1933, 1463.

[52b] R. Robinson, *J.*, 1936, 80.

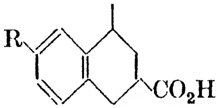
[53] J. W. Cook and C. A. Lawrence, *ibid.*, p. 1431.

* It appears to the Reporter that in view of Meerwein's observations of the rearrangements accompanying the dehydration of 2 : 2-dimethyl*cyclo*hexanol, the formulæ given above for dehydration and cyclo-dehydration products of disubstituted alcohols of this type are open to suspicion, unless confirmed by some analytical method.

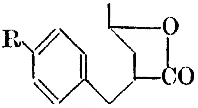
sider under this heading the cyclisation or attempted cyclisation, by the same general method, of compounds containing carbonyl, carboxyl, carbethoxyl and similar groups. As has already been stated, the main advances in this field are due to G. Darzens and his collaborators, particularly A. Lévy. The typical Darzens synthesis [54] proceeds as follows: Benzylallylmalonic ester, prepared by successive benzylation and allylation of malonic ester, is hydrolysed and decarboxylated to benzylallylacetic acid (LV, R = H). This, on treatment with 78% sulphuric acid below 45°, yields a mixture of the corresponding acid derived from tetralin (LVI, R = H) and the lactone (LVII, R = H), both of which are isomeric with (LV). It was at first thought that the lactone



(LV.)



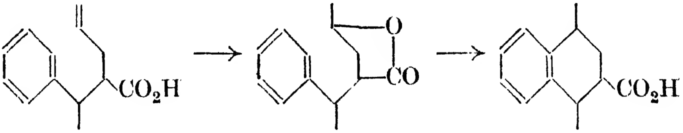
(LVI.)



(LVII.)

(LVII, R = H) could not be cyclised similarly, but later [55] it was found that 65% sulphuric acid at 120° slowly converted it into the dicyclic acid (LVI). As a corollary the unsaturated acid gives an excellent yield of (LVI) under these conditions. The method is well adapted for the synthesis of acids derived from alkyl tetralins and naphthalenes and of alkyl naphthalenes. Thus the acid (LVI, R = H) on dehydrogenation with sulphur and decarboxylation with lime yields successively 1-methyl-3-naphthoic acid and 1-methylnaphthalene.

The reaction (LV ⟶ LVI) appears to be general for this type of unsaturated acid. It has been observed in the cases when R = Me,[56] $CHMe_2$,[57] CMe_3,[58] and OMe,[59] and also [60] in the cyclisation:



(LVIII.) (LIX.)

There were minor differences in the conditions (time, concentration of acid, temperature) used for the cyclisations of the various acids and lactones, but the products were of the same type and could be degraded to alkyl naphthalenes in the same manner.

[54] G. Darzens, *Compt. rend.*, 1926, **183**, 748, 1110.

[55] *Ibid.*, 1930, **190**, 305.

[56] G. Darzens and A. Heinz, *Compt. rend.*, 1927, **184**, 33.

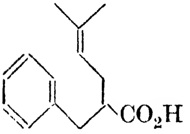
[57] G. Darzens and A. Lévy, *ibid.*, 1932, **194**, 2056.

[58] *Ibid.*, 1934, **199**, 1426.

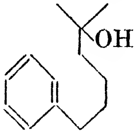
[59] *Ibid.*, 1935, **200**, 469.

[60] G. Darzens, *ibid.*, 1930, **190**, 1562.

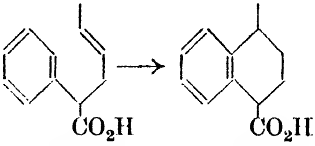
In this way the product (LVI, R = $CHMe_2$) yielded eudalene,[57] the dehydrogenation product of the eudesmol group of sesquiterpenes. The only acid of the type which failed to cyclise by this reaction was (LX).[61] It is instructive to contrast this with the behaviour of the alcohol (LXI), which yields 1-*iso*propyltetralin on cyclo-dehydration.[27] The carboxyl group appears to inhibit cyclisation.



(LX.)



(LXI.)

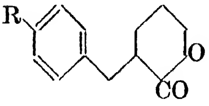


(LXII.) (LXIII.)

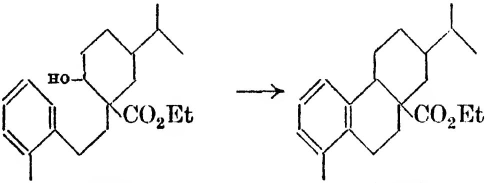
Although the reaction has been mainly observed with compounds containing the acid group in the β-position, one such cyclisation of an α-acid (LXII ⟶ LXIII) occurs, although slowly.[62] The reaction has also been applied to syntheses of hydrophenanthrene derivatives,[63] and from these 1-methyl- and 1 : 9-dimethyl-phenanthrenes have been prepared.

Some of the lactonisations of the unsaturated acids encountered in the course of this work were interesting. For instance, the acid (LVIII) lactonised so readily that it had no sharp boiling point. This contrasts with the parent acid, allylacetic acid, which shows little tendency to lactonise at the boiling point.[64] In certain instances,[57, 59] treatment of the unsaturated acid with sulphuric acid yielded as by-product not only the γ-lactone (type LVII) but the isomeric δ-lactone (type LXIV). Unlike the γ-lactones, the δ-lactones failed to cyclise to tetralin derivatives. The formation of a δ-lactone also provides a difference from allylacetic acid, which yields only a γ-lactone.[64]

Some of the syntheses of Bardhan and Sengupta [31] involve the cyclo-dehydration of esters of aromatic hydroxy-acids, for example, (LXV ⟶ LXVI) :



(LXIV.)



(LXV.) (LXVI.)

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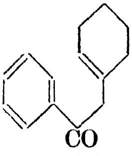
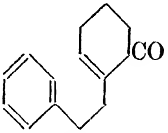
[61] G. Darzens and A. Lévy, *Compt. rend.*, 1930, **191**, 1455.
[62] G. Darzens and A. Lévy, *ibid.*, 1934, **199**, 1131.
[63] *Ibid.*, 1935, **200**, 2187; 1936, **202**, 427.
[64] R. P. Linstead and H. N. Rydon, *J.*, 1933, 580.

Similar cyclisations of esters are to be found in the work of R. D. Haworth and his collaborators.[65] These reactions involve essentially the ring closure of a compound with the double bond αβ (or βγ) to the functional group, as against the γδ-compounds of Darzens.

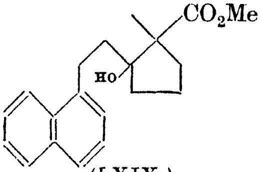
Against these positive results we may set the apparent inability of many unsaturated hydroaromatic ketones to cyclise, for example, (LXVII),[38] (LXVIII) and similar ketones.[66] The hydroxy-ester (LXIX) resists cyclisation by a variety of reagents.[67] On the other hand, a number of aromatic diketones and ketonic esters, probably functioning as *unsaturated* hydroxy-ketones and unsaturated hydroxy-esters, form polycyclic compounds with ease (see Method 5).



(LXVII.)



(LXVIII.)



(LXIX.)

(4) *Cyclisations involving Double Bonds in Different Molecules. Diene Synthesis.*

A logical extension of methods (2) and (3) is the union of two separate unsaturated molecules to form a ring. The only effective method of carrying this out is by the diene synthesis. This has already been reviewed in these Reports and we shall mention only its application to hydrophenanthrene and hydroanthracene systems.

The condensation of dienes with quinones, discovered by H. von Euler and K. O. Josephson,[68] and extensively investigated by O. Diels and K. Alder,[69] can be applied to the preparation of polycyclic compounds containing angular methyl groups. Thus Erich Adler [70] condensed *p*-xyloquinone with butadiene in benzene at 160—170° to dimethyloctahydroanthraquinone (LXX), but the yield was poor and there seems no doubt that methyl groups inhibit this type of condensation.[71]

The main application of the diene synthesis to the hydrophenanthrene and related fields is due to L. F. Fieser and his co-workers. It was first found [72] that benzoylacrylic acid (LXXI),

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[65] *E.g.*, R. D. Haworth, C. R. Mavin, and G. Sheldrick, *J.*, 1934, 454.

[66] A. Cohen and J. W. Cook, *J.*, 1935, 1570.

[67] R. Robinson and J. Walker, *ibid.*, p. 1530.

[68] *Ber.*, 1920, **53**, 822.

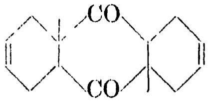
[69] See *Ann. Reports*, 1930, **27**, 88.

[70] *Arkiv Kemi, Min., Geol.*, 1935, **11**, *B*, No. 49, 1.

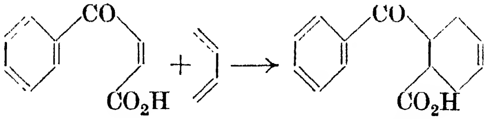
[71] Cf. C. K. Chuang and C. T. Han, *Ber.*, 1935, **68**, 876.

[72] L. F. Fieser and (Mrs.) M. Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 1679.

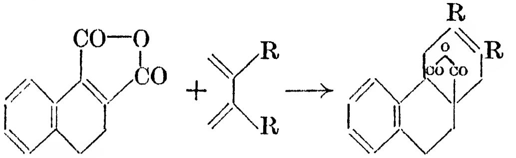
which is easily obtained from benzene and maleic anhydride, condensed smoothly with butadiene in alcohol at 100° to yield benzoyltetrahydrobenzoic acid (LXXII). This substance and its derivatives do not cyclise readily, but after dehydrogenation with sulphur (in the form of esters) yield *o*-benzoylbenzoic acids, which, as is well known, give anthraquinones with great ease. Only one successful formation of a hydrophenanthrene derivative from a β-naphthaquinone has been reported,[73] but the 'maleic anhydrides' of the hydronaphthalene series, such as (LXXIII), react smoothly with dienes,[74] thus :



(LXX.)



(LXXI.) (LXXII.)



(LXXIII.)

(R = H, Me)

The dimethyl ester corresponding to the product (R = Me) is exceedingly resistant to hydrolysis. Treatment of the unsaturated anhydride with selenium appears to lead to a reversal of the diene synthesis. Decarboxylation by alkali at a high temperature yields a mixture of hydrophenanthrenes. The method is not suitable for the production of pure hydrophenanthrenes, but is well adapted to the preparation of their aromatic dehydrogenation products.

The corresponding chrysene derivatives have also been synthesised and similar condensations have been effected with cyclic dienes.[75] The scope of the process has been extended [76] by the development of a method for the preparation of the necessary intermediates of type (LXXIII). This is described later. An even milder reaction has been realised by L. F. Fieser and H. L. Holmes,[77] who have succeeded in adding dienes to esters of dihydronaphthalene *mono*-carboxylic acids. Condensation is slow, but the products (LXXIV) can easily be isolated owing to their resistance to hydrolysis and can be dehydrogenated to phenanthrenes.

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[73] L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, 1934, **56**, 2690.

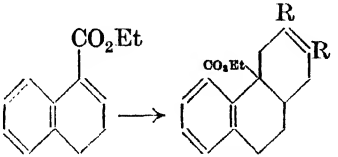
[74] L. F. Fieser and E. B. Hershberg, *ibid.*, 1935, **57**, 2192.

[75] L. F. Fieser, M. Fieser, and E. B. Hershberg, *ibid.*, 1936, **58**, 1463.

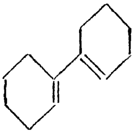
[76] L. F. Fieser and E. B. Hershberg, *ibid.*, p. 2315.

[77] *Ibid.*, p. 2319.

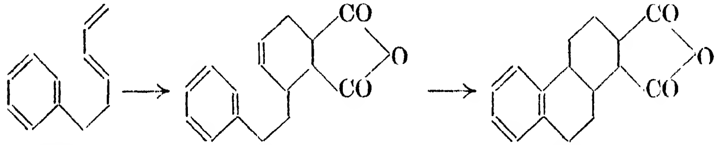
The reverse of this method, namely, the addition of maleic anhydride or a similar compound to a dicyclic or potentially dicyclic hydrocarbon containing a diene unit, has been used by E. de Barry Barnett and C. A. Lawrence [78] and by E. E. Gruber and R. Adams.[79] The English workers dehydrated the pinacol derived from *cyclo*hexanone to the diene (LXXV), which yielded additive products of the usual type with maleic anhydride, benzoquinone and α-naphthaquinone. Gruber and Adams independently studied the addition of maleic anhydride and of acraldehyde to this diene. A. Cohen [80] has examined the parallel route (LXXVI ⟶ LXXVII ⟶ LXXVIII), but the process is not general. The unsubstituted compounds cyclised in the manner shown, but the methoxy-derivatives gave polymeric products. More recently, the same author [81] has reported similar condensations from 1-vinylnaphthalene and its 6-methoxy-derivative. These with maleic anhydride yield the corresponding dihydrophenanthrenedicarboxylic anhydrides. One of the particular objects of this work has been the preparation of synthetic oestrogenic compounds.



(LXXIV.)



(LXXV.)



(LXXVI.) (LXXVII.) (LXXVIII.)

(5) *Cyclo-dehydration of Ketonic Esters and Diketones.*

(*a*) *Ketonic Esters.*—There have been two distinct lines of development, that leading to the fusion of two alicyclic rings and that involving one aromatic ring. The basis of the first method is the formation of a dicyclic dihydroresorcinol by the Michael addition of malonic ester to a cyclic unsaturated ketone (or of acetoacetic ester to a cyclic unsaturated ester), followed by the spontaneous closure of the second ring, under the conditions of reaction, and by

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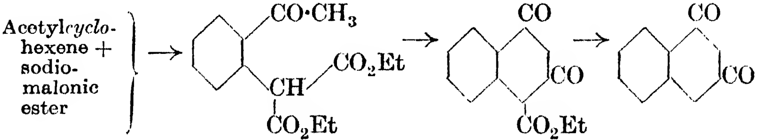
[78] *J.*, 1935, 1104.

[79] *J. Amer. Chem. Soc.*, 1935, **57**, 2555.

[80] *J.*, 1935, 429.

[81] A. Cohen, *Nature*, 1935, **136**, 869.

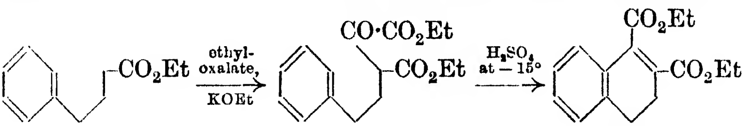
hydrolysis. The first application of this method was P. Rabe's synthesis of a diketo-octahydrophenanthrene,[33] and the simplest example is the preparation of 1 : 3-diketodecalin by G. A. R. Kon and M. Qudrat-i-Khuda : [82]



(LXXIX.)

This method was further studied by L. Ruzicka, D. R. Koolhaas, and A. H. Wind,[83] who used it for the preparation of various alkyl decalins allied to the hydrogenated sesquiterpenes of the selinene class. The natural products, however, contain a *cis*-locking of the rings, the synthetic, a *trans*-locking; for example, the diketone (LXXIX) yields oxidation products undoubtedly belonging to the *trans*-series.[82, 84] More recently [85] this diketone has been isolated in both *cis*- and *trans*-forms. It appears that the initial addition yields a *cis*-keto-ester, that mild hydrolysis of this gives a *cis*-diketone, whereas hydrolysis with hot alkali causes an isomeric change to the *trans*-diketone. The corresponding compounds containing a 9-(angular) methyl group have also been investigated.[83, 86, 87] Here again there is evidence from oxidation of the existence of *cis*- and *trans*-isomerides.[87] The corresponding dione of the hydrindane series appears to be stable in the *cis*-form,[88] in agreement with theory.

The pioneer work on the preparation of polycyclic compounds by the dehydration of ketonic esters of the aromatic series was that of J. Bougault [89] and K. von Auwers and K. Möller.[90] Bougault discovered that the condensation product from β-phenylpropionic ester and oxalic ester yielded the diester of indene-1 : 2-dicarboxylic acid when treated with sulphuric acid. Von Auwers and Möller applied the method to the hydronaphthalene series as follows :



(LXXIXa.)

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[82] *J.*, 1926, 3071. [83] *Helv. Chim. Acta*, 1931, **14**, 1151.

[84] J. W. Barrett, A. H. Cook, and R. P. Linstead, *J.*, 1935, 1066.

[85] C. K. Chuang and Y. L. Tien, *Ber.*, 1936, **69**, 25.

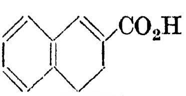
[86] G. R. Clemo and H. G. Dickenson, *J.*, 1935, 735.

[87] R. P. Linstead and A. F. Millidge, *J.*, 1936, 478.

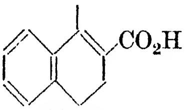
[88] C. K. Chuang, C. M. Ma, and Y. L. Tien, *Ber.*, 1935, **68**, 1946.

[89] *Compt. rend.*, 1915, **159**, 745. [90] *J. pr. Chem.*, 1925, [ii], **109**, 124.

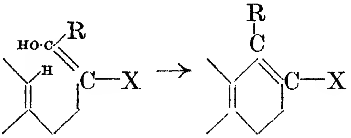
If the final cyclisation were carried out at room temperature, the anhydride corresponding to (LXXIX*a*) was obtained. The α-formyl and acetyl derivatives of γ-phenylbutyric ester were condensed similarly to (LXXX) and (LXXXI) respectively.[90] Such reactions



(LXXX.)



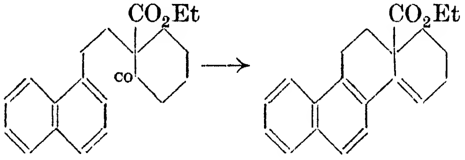
(LXXXI.)



may be considered as cyclo-dehydrations of the enolic forms of the keto-esters, as shown in a generalised form above, where X = CO_2Et and R = H, Me or CO_2Et.

The first use of such a reaction for the synthesis of substances with a sterol-like skeleton was that of L. Ruzicka, L. Ehmann, M. W. Goldberg, and H. Hösli.[91] They condensed β-1-naphthylethyl bromide with *cyclo*hexanone-*o*-carboxylic ester and cyclised the product (LXXXII) by boiling 50% sulphuric acid to the hydrochrysene ester (LXXXIII), which yielded chrysene on dehydrogenation. The method was also used for the synthesis of *cyclo*-pentenophenanthrene derivatives. The use of stronger acid led to removal of the carbethoxyl group and some dehydrogenation.

(LXXXII.)



(LXXXIII.)

An ingenious application of the method is due to J. C. Bardhan,[92] who has condensed naphthylethyl bromide with the sodio-derivative of β-ketoadipic ester and cyclised the product (LXXXIV) to dihydrophenanthrene-1-propionic-2-carboxylic acid (LXXXV). The advantage of this process is that it leads to the synthesis of an α-ketone (such as LXXXVI), resembling equilenin (LXXXVII).

A method similar to that of Ruzicka has been used by J. W. Cook and his collaborators for the preparation of naphtha(1′ : 2′ : 2 : 3)-fluorene,[93] and for that of cholanthrene from 1-iodoacenaphthene.[94]

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[91] *Helv. Chim. Acta*, 1933, **16**, 833.

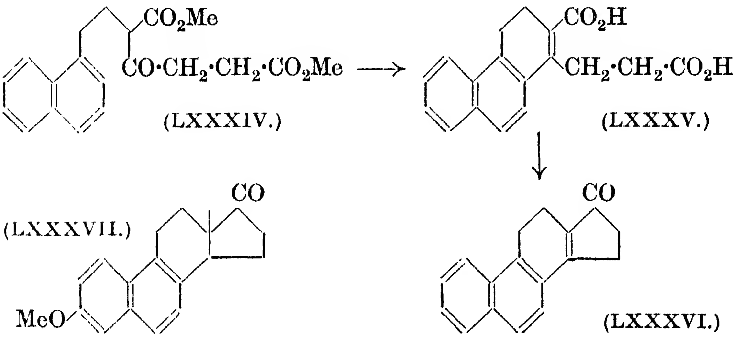
[92] *Nature*, 1934, **134**, 217; *Chem. and Ind.*, 1936, **55**, 879; *J.*, 1936, 1848.

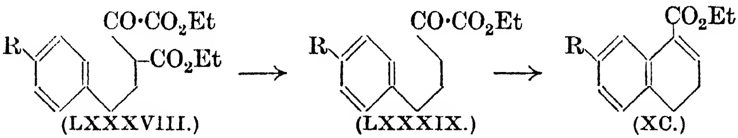
[93] J. W. Cook, A. Dansi, C. L. Hewett, J. Iball, W. V. Mayneord, and (Miss) E. Roe, *J.*, 1935, 1319.

[94] J. W. Cook, G. A. D. Haslewood, and (Mrs.) A. M. Robinson, *J.*, 1935, 667.

In the latter synthesis, the concentration of sulphuric acid used in the cyclisation was very critical, and the process has its limitations.[93]

The Bougault reaction has been studied by L. F. Fieser and E. B. Hershberg.[95, 96] By condensing γ-1- and -2-naphthylbutyric esters with oxalic ester and cyclising the products, they were able to prepare the anhydrides of two dihydrophenanthrene-*o*-dicarboxylic acids.[88] Various methoxyl derivatives of dihydronaphthalene- and phenanthrene-dicarboxylic acids have been prepared by essentially the same process.[96, 97] For the preparation of substituted dihydronaphthoic esters, required for condensation with dienes (see Method 4), L. F. Fieser and H. L. Holmes [98] modified the reaction as follows: The oxalyl ester (such as LXXXVIII) was hydrolysed by 15% sulphuric acid to the corresponding glyoxylic ester (LXXXIX). This on treatment with 65% acid yielded the dicyclic ester (XC).





(*b*) *Diketones.*—The developments in this field are mainly due to the work of R. Robinson and his collaborators.

The first synthesis of a dicyclic compound involving the cyclisation of a 1 : 5-diketone seems to be that recorded by J. W. Barrett, A. H. Cook, and R. P. Linstead,[84] who observed that ethyl sodioacetoacetate reacted with acetyl*cyclo*hexene to yield, by Michael addition and subsequent cyclisation, the unsaturated dicyclic

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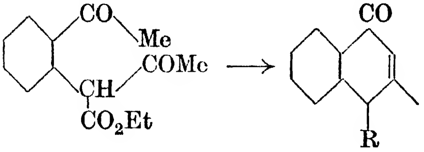
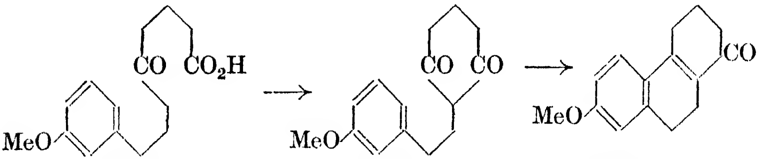
[95] *J. Amer. Chem. Soc.*, 1935, **57**, 1851.
[96] *Ibid.*, 1936, **58**, 2315.
[97] A. Cohen, J. W. Cook, and C. L. Hewett, *J.*, 1936, 52.
[98] *J. Amer. Chem. Soc.*, 1936, **58**, 2319.

ketone (XCI, R = H), together with its carbethoxyl derivative ($R = CO_2Et$). The products belonged to the *trans*-series.

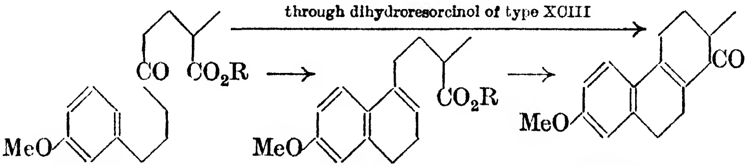


(XCI.)



(XCII.) (XCIII.) (XCIV.)

In a most ingenious series of experiments, R. Robinson and E. Schlittler [99] condensed the chloride of γ-*m*-methoxyphenylbutyric acid * with ethyl sodio-α-acetylglutarate to yield a product hydrolysing to the δ-keto-acid (XCII). The methyl ester of this yielded the corresponding dihydroresorcinol (XCIII) with sodium ethoxide. This, on dehydration with phosphoric oxide, was cyclised to the unsaturated mono-ketone (XCIV). The corresponding alcohol on dehydrogenation and methylation yielded 1 : 7-dimethoxyphenanthrene. The cyclisation of this 1 : 5-diketone resembles the Bougault reaction, and presumably, like it, involves the dehydration of an enol. C. L. Hewett [1] has obtained the same ketone (XCIII) by direct substitution of dihydroresorcinol and has confirmed its cyclodehydration. Unfortunately, *O*-alkylation complicated this method of preparation.



(XCV.) (XCVI.) (XCVII.)

R. Robinson and J. Walker [2] have extended the Robinson–Schlittler method to the preparation of (XCVII), the methyl derivative of (XCIV), from the corresponding δ-keto-ester (XCV).

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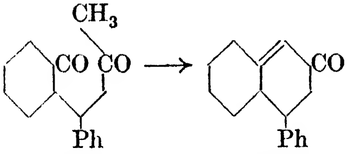
[99] *J.*, 1935, 1288. [1] *J.*, 1936, 50. [2] *J.*, 1936, 192.

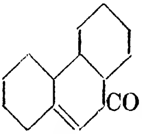
* The best method of preparing this important intermediate, first obtained by Henry W. Thompson (*J.*, 1932, 2310), is in doubt. See ref. (99), and C. K. Chuang and Y. T. Huang, *Ber.*, 1936, **69**, 1505; E. L. Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

The position was consolidated by the cyclo-dehydration of the keto-ester (XCV) by cold sulphuric acid to the dihydronaphthalene derivative (XCVI). The corresponding acid chloride gave the same unsaturated ketone (XCVII) on cyclisation with stannic chloride. The reduction of (XCIV) has been examined by the same investigators,[3] who have succeeded in converting it, by oxidising the corresponding saturated alcohol with Beckmann's mixture, into the important 1-keto-7-methoxytetrahydrophenanthrene of A. Butenandt and G. Schramm (see later). The decalin system present in the reduction products of (XCIV) has been obtained in both *cis*- and *trans*-forms.

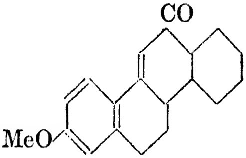
Another line of attack used by the same school consists in the addition of the sodio-derivative of a saturated ketone to an αβ-unsaturated ketone with the formation of a 1 : 5-diketone, followed by spontaneous cyclo-dehydration of the latter, following H. Stobbe.[3a] Thus, sodio*cyclo*hexanone condenses with styryl methyl ketone to give first a saturated 1 : 5-diketone (XCVIII), and then an unsaturated dicyclic ketone (XCIX). The reaction is general; acetyl*cyclo*hexene and *cyclo*hexanone yield as final product the dodecahydrophenanthrone[4] (C), and 6-methoxy-1-tetralone and acetyl*cyclo*hexene, the chrysene derivative (I). The tetrahydro-derivative of (I) is an alcohol and *X*-ray analysis[5] supports its formulation as a hydroxyhydrochrysene. The keto-hydrochrysenes similarly obtained from α-tetralone and acetyl*cyclo*hexene have been investigated in detail by D. A. Peak and R. Robinson,[6] and the corresponding hydro*cyclo*pentenophenanthrene derivatives have also been examined.[7]



(XCVIII.) (XCIX.)

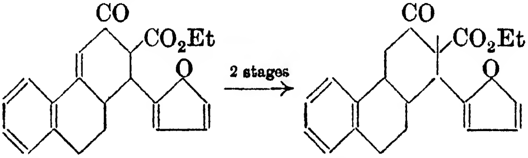


(C.)



(I.)

(II.)



(III.)

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[3] *J.*, 1936, 747. [3a] *J. pr. Chem.*, 1912, **86**, 209.

[4] W. S. Rapson and R. Robinson, *J.*, 1935, 1285.

[5] (Miss) D. Crowfoot, W. S. Rapson, and R. Robinson, *J.*, 1936, 757.

[6] *Ibid.*, p. 759.

[7] J. R. Hawthorne and R. Robinson, *ibid.*, p. 763.

A modification of the Knoevenagel synthesis of *cyclo*hexenones has been described,[8] in which the keto-ester (II) is prepared either by condensing ethyl furfurylideneacetoacetate with α-tetralone or, better, from 2-furfurylidene-α-tetralone and ethyl acetoacetate. The dihydro-compound of this can be methylated to the keto-ester (III). The function of the furyl radical in this work is to act as the source of a carboxyl group or of a side chain terminated by carboxyl.

These interesting researches probably represent the nearest approach as yet realised to a synthesis of oestrone. Some further methods now under investigation are outlined by R. Robinson in the fifth Pedler Lecture.[9]

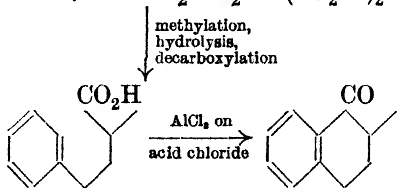
(6) *Formation of Cyclic Ketones from Monocarboxylic Acids and their Derivatives.*

In this group is considered the formation of cyclic ketones by the dehydration of acids, or by loss of hydrogen chloride from acid chlorides. The most important examples are those in which an aromatic ring provides the centre which is attacked by the acid or acid chloride group. In the latter case the reaction is an internal Friedel–Crafts condensation. Recently it has been found that alicyclic rings can undergo a similar reaction; this aspect is considered later.

It will be impossible to enumerate all the applications of the reaction in the aromatic field; the following are the most important from the present point of view. The typical reaction is the formation of α-hydrindone from β-phenylpropionyl chloride discovered by F. S. Kipping. The process was soon applied to the synthesis of α-ketotetrahydronaphthalenes (α-tetralones). Thus G. Schroeter, L. Lichtenstadt, and D. Irineu [10] prepared β-methyl-α-tetralone (V) by the representative series of reactions :

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2Br} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2}$$

(IV.)



(V.)

F. Krollpfeiffer and W. Schäfer [11] prepared this and similar tetralones, using sulphuric acid for the final ring closure. The necessary

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[8] D. A. Peak, R. Robinson, and J. Walker, *J.*, 1936, 752.

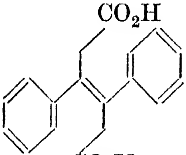
[9] *J.*, 1936, 1079.

[10] *Ber.*, 1918, **51**, 1599.

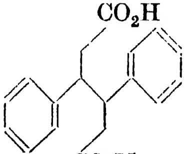
[11] *Ber.*, 1923, **56**, 620; compare a series of papers by A. Stevenson, J. F. Thorpe, and co-workers, *J.*, 1923, **123**, 1755, etc.

phenylbutyric acids were made by Clemmensen reduction of the corresponding benzoylpropionic acids, themselves prepared by the condensation of succinic anhydrides with aromatic hydrocarbons or of sodiomalonic esters with bromo-ketones such as ω-bromoacetophenone.[12] The fundamental structural aspects of the reaction were examined by J. von Braun and G. Manz.[13] They found that, in competitive reactions, the tetralone system was formed more readily than the hydrindone, and this more readily than the benzsuberone. The methods described in these papers have provided the basis for one well-recognised method for the synthesis of aromatic compounds. For this purpose it is usual either to reduce the hydroaromatic ketone and dehydrogenate the product, or to subject the ketone to the Grignard reaction and dehydrogenate the tertiary alcohol so obtained, or its dehydration product. In this way a large number of substituted naphthalenes and phenanthrenes have been prepared, particularly by L. Ruzicka, R. D. Haworth, and their collaborators.[14]

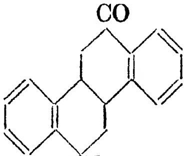
The first application to the tricyclic series was due to G. Schroeter,[15] and tetracyclic compounds were first prepared by E. Beschke,[16] and J. von Braun and G. Irmisch.[17] Beschke applied the Reformatsky reaction to benzil and performed a double ring closure on the dibasic acid (VI). Von Braun and Irmisch obtained the *meso-* and racemic forms of the diketohexahydrochrysene (VIII) by internal Friedel–Crafts reactions on the acid chlorides of *meso-* and racemic βγ-diphenyladipic acids (VII).



(VI.)



(VII.)



(VIII.)

More recently it has been found that the two saturated acids or their esters are readily cyclised by hot 85% sulphuric acid.[18] The

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[12] Compare also F. Mayer and G. Stamm, *Ber.*, 1923, **56**, 1424.

[13] *Annalen*, 1929, **468**, 258; and other papers by von Braun; compare also A. F. Titley, *J.*, 1928, 2571, etc.

[14] *Ann. Reports*, 1932, **29**, 152; for recent work see L. Ruzicka, H. Hösli, and K. Hofmann, *Helv. Chim. Acta*, 1936, **19**, 370.

[15] *Ber.*, 1924, **57**, 2003, 2025; G. Schroeter, H. Müller, and J. V. S. Huang, *ibid.*, 1929, **62**, 645.

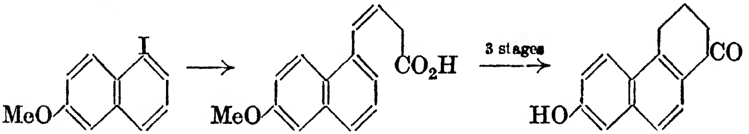
[16] *Annalen*, 1911, **384**, 143.

[17] *Ber.*, 1931, **64**, 2461.

[18] G. R. Ramage and R. Robinson, *J.*, 1933, 607.

ketones are stable and yield homogeneous hexahydrochrysenes on reduction, both of which yield chrysene with selenium.[18] The configurations of the parent acids are known,[19] and from this the *cis*- and *trans*-arrangements of the two central rings follow. This work has been followed up by H. J. Lewis, G. R. Ramage, and R. Robinson;[20] but the main difficulty is the preparation of suitably substituted βγ-diphenyladipic acids, for the yield of these from the bimolecular reduction of substituted cinnamic esters is poor.

Two important syntheses have been carried out by the general route by A. Butenandt and his co-workers. In the first[21] 1 : 2-dimethylphenanthrene was prepared by the Schroeter–Haworth method, and was found to be identical with that obtained by the degradation of oestrone and ætiobilianic acid. The second[22] was concerned with the preparation of 1-keto-7-hydroxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (XI), which will probably prove to be a key-intermediate in the synthesis of equilenin. A novelty in this process was the method used for the introduction of the butyric acid side chain. The Grignard compound of 1-iodo-6-methoxynaphthalene (IX) was condensed with succinic half-aldehyde, half-ester, or with the product formed from the addition of methylmagnesium iodide to succinic acid ester. This yielded the methoxynaphthylbutenoic acid (X), from which the desired phenolic ketone (XI) was obtained by reduction, cyclisation (with stannic chloride), and demethylation. The general interest attaching to these compounds is reflected in the fact that three other preparations of the methoxy-derivative of (XI) have since been reported. A slightly modified preparation is described by A. Cohen, J. W. Cook, and C. L. Hewett,[23] and Robinson and Walker's synthesis of the same compound has already been mentioned.[2] G. Haberland's recent synthesis[24] differs from that of Butenandt and Schramm mainly in the use of tetralin derivatives in place of naphthalene. 6-Methoxy-1-tetralone (XII) was subjected to the Reformatsky reaction and the unsaturated esters so obtained were reduced by the Bouveault–Blanc process to



(IX.) (X.) (XI.)

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[19] (Miss) M. Oommen and A. I. Vogel, *J.*, 1930, 2148.

[20] *J.*, 1935, 1412.

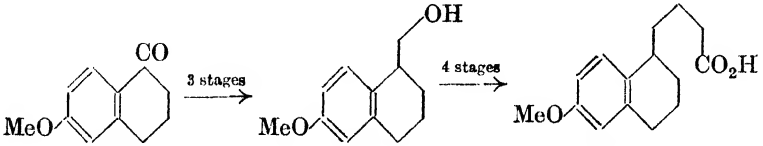
[21] A. Butenandt, H. A. Weidlich, and H. Thompson, *Ber.*, 1933, **66**, 601.

[22] A. Butenandt and G. Schramm, *Ber.*, 1935, **68**, 2083.

[23] *J.*, 1936, 53.

[24] *Ber.*, 1936, **69**, 1380.

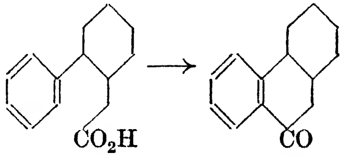
the corresponding ethanol (XIII). The bromide of this by the malonic ester synthesis gave the acid (XIV), which on dehydrogenation with sulphur yielded 6-methoxynaphthylbutyric acid (dihydro-derivative of X). The cyclisation of this to the methoxy-ketone was achieved with 90% sulphuric acid.



(XII.) (XIII.) (XIV.)

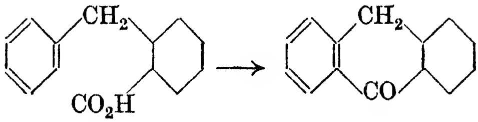
An interesting paper[25] by J. W. Cook, C. L. Hewett, and C. A. Lawrence deals with the preparation of stereoisomeric 2-phenyl-*cyclo*hexylacetic acids (XV) from 2-phenyl*cyclo*hexanone and their cyclisation to keto-octahydrophenanthrenes (XVI), and with analogous experiments on the cyclisation of hexahydrobenzylbenzoic acids to keto-octahydroanthracenes (XVII ⟶ XVIII).

(XV.)



(XVI.)

(XVII.)



(XVIII.)

Diphenyl-2-acetic acid itself yields 9-hydroxyphenanthrene on cyclo-dehydration.[26]

Among miscellaneous syntheses which have involved this method of cyclisation are three in the 1 : 2-*cyclo*pentenophenanthrene-series,[45, 27, 27a] that of 1 : 2-benzpyrene,[28] and that of octahydrodibenzanthrone.[29] Two different syntheses of cholanthrene by its use have been reported.[30] The use of veratrole as a starting material has been explored.[31] A promising route appeared to be

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[25] *J.*, 1936, 71.

[26] N. N. Chatterjee, *J. Indian Chem. Soc.*, 1935, **12**, 591; compare I. R. Sherwood, W. F. Short, and J. Woodcock, *J.*, 1936, 322.

[27] W. E. Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 1381.

[27a] H. Hillemann, *Ber.*, 1936, **69**, 2610.

[28] A. Winterstein, H. Vetter, and K. Schön, *Ber.*, 1935, **68**, 1079.

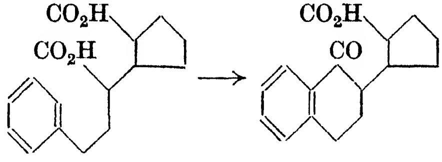
[29] E. de B. Barnett, N. F. Goodway, and C. A. Lawrence, *J.*, 1935, 1684.

[30] J. W. Cook and G. A. D. Haslewood, *J.*, 1935, 767, 770.

[31] R. Robinson and P. C. Young, *ibid.*, p. 1414.

blocked when it was found [32] that, although the dicarboxylic acid (XIX) could be cyclised to the keto-acid (XX), the ester of this failed to undergo the Reformatsky reaction. The synthesis of a compound containing the skeleton of the revised (tricyclic) formula for vitamin-D_2 is reported.[33] Two methylmethoxyphenanthrenes have been prepared by the Schroeter–Haworth process.[34]

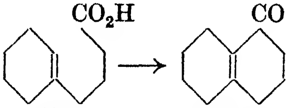
(XIX.)



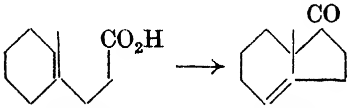
(XX.)

Cyclisation involving Non-aromatic Rings.—It is well known that G. Darzens demonstrated that acid chlorides could be condensed with unsaturated alicyclic hydrocarbons by a reaction resembling that of Friedel and Crafts. This at once indicates the possibility of the internal condensation of γδ- or δε-unsaturated acids, or their chlorides, to unsaturated ketones. Nevertheless it is not to be expected that the reaction will proceed so smoothly as its aromatic counterpart because of the danger of polymerisation and lactonisation.

Cyclisations of this type were first realised independently by J. W. Cook and C. A. Lawrence,[35] and R. Robinson and J. Walker.[2] The latter work has already been mentioned; the former consisted in the preparation of $\Delta^{9:10}$-α-octalone (XXII) from Δ^1-*cyclo*hexenylbutyric acid (XXI). The ketone was identical with that prepared by W. Hückel and H. Naab [36] by the oxidation of $\Delta^{9:10}$-octalin. An interesting paper by C. K. Chuang, Y. L. Tien, and C. M. Ma [37] describes the synthesis of α-ketones containing angular methyl groups by the same process. Thus, 8-methyl-1-hydrindenone (XXIV, position of double bond uncertain) was prepared from 2-methyl-Δ^1-*cyclo*hexenylpropionic acid (XXIII).



(XXI.) (XXII.)



(XXIII.) (XXIV.)

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[32] W. S. Rapson and R. Robinson, *J.*, 1935, 1533.

[33] S. Natelson and S. P. Gottfried, *J. Amer. Chem. Soc.*, 1936, **58**, 1432.

[34] P. Hill, W. F. Short, and (Miss) A. Higginbottom, *J.*, 1936, 317; W. F. Short, H. Stromberg, and A. E. Wiles, *ibid.*, p. 319.

[35] *J.*, 1935, 1637.

[36] *Annalen*, 1933, **502**, 153.

[37] *Ber.*, 1936, **69**, 1494.

Reduction of the latter gave the corresponding saturated ketone, the structure of which was shown by its oxidation to methyl*cyclo*hexane-1-carboxylic-2-acetic acid, which had already been synthesised.[38, 87] A similar synthesis of 9-methyl-1-decalone has been reported,[37] but in this case the structure of the product has not yet been proved.

(7) *Formation of Cyclic Ketones from Dibasic Acids.*

The formation of cyclic ketones from dibasic acids can be effected by distillation of the barium salts, distillation of the acids with acetic anhydride or with a trace of baryta, or from the esters by the Dieckmann reaction. These processes have been widely used in the preparation of dicyclic ketones[39] but have not so far been of much service in more complex cases. We need only mention here F. Vocke's valuable study of the pyrolysis of reduced diphenic acids,[40] the synthetic experiments of J. C. Bardhan and S. K. Banerji in the cadinene group of sesquiterpenes,[41] and the unusual ketonisation observed by A. E. Bradfield, E. R. Jones, and J. L. Simonsen.[42]

Owing to the rapid growth of the subject and the large number of workers involved, the Reporter has been conscious of unusual difficulty in trying to preserve a proper balance between the various developments and in assigning priority. The literature has been reviewed up to and including December, 1936.

R. P. L.

7. Natural Products of the Sterol Group.

(Continued from *Ann. Reports*, 1933, **30**, 198; 1934, **31**, 206.)

Investigations of natural products derived from *cyclo*pentanoperhydrophenanthrene have shown undiminished activity, and early in 1936 two excellent monographs[1, 2] were published. To these reference should be made for more detailed information.

Sterols.

The preparation of an interesting series of isomerides of cholesterol (I) has now been completed. R. Schoenheimer and E. A. Evans[3]

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[38] C. K. Chuang, Y. L. Tien, and Y. T. Huang, *Ber.*, 1935, **68**, 864.

[39] See *Ann. Reports*, 1935, **32**, 305.

[40] *Annalen*, 1934, **508**, 1.

[41] *J.*, 1935, 476.

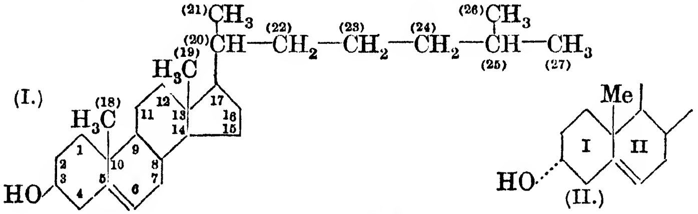
[42] *J.*, 1936, 1137.

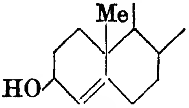
[1] L. F. Fieser: "The Chemistry of Natural Products related to Phenanthrene." American Chemical Society Monograph Series, No. 70.

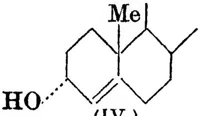
[2] H. Lettré and H. H. Inhoffen: "Über Sterine, Gallensäuren und verwandte Naturstoffe." Verlag von Ferdinand Enke in Stuttgart.

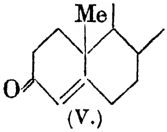
[3] *J. Amer. Chem. Soc.*, 1936, **58**, 182; *J. Biol. Chem.*, 1936, **114**, 567.

have shown that the substance to which the structure of *allo*cholesterol (III) was formerly attributed is a mixture of (I) and (III). By reduction of cholestenone (V) with aluminium *iso*propoxide, these authors obtained an addition compound of *allo*cholesterol with *epiallo*cholesterol (IV). As only the former is precipitated by digitonin, both (III) and (IV) could be isolated in the pure state. The properties of pure *allo*cholesterol are quite different from those inferred from a study of the mixture of (I) and (III), which led, for example, to the erroneous conclusion[4] that *allo*cholesterol is easily isomerised to cholesterol. Finally, *epi*cholesterol (II) has been obtained[5] by the action of oxygen on a Grignard solution prepared from cholesteryl chloride. This gave a mixture of cholesterol and *epi*cholesterol, from which the latter was isolated by precipitating the cholesterol with digitonin.


(I.)
(II.)


(III.)


(IV.)


(V.)

Cholesterol and *epi*cholesterol are hydrogenated to cholestanol and *epi*cholestanol (*trans*-fusion of rings I and II), respectively, whereas *allo*cholesterol gives coprosterol (coprostanol) (*cis*-fusion of rings I and II) and *epiallo*cholesterol gives a mixture of *epi*cholestanol and *epi*coprostanol. A striking property of all of the three new isomerides of cholesterol (II, III, and IV) is the ease with which they become dehydrated by dilute alcoholic hydrochloric acid. This leads, in the case of (III) and (IV) to $\Delta^{2:4}$-cholestadiene, the absorption spectrum of which resembles that of ergosterol, although the bands are displaced farther into the ultra-violet. The influence of the $\Delta^{5:6}$-double bond on the *epi*-hydroxyl group of *epi*cholesterol is very remarkable; it was found independently by J. H. Beynon, I. M. Heilbron and F. S. Spring[6] that a similar lability is shown

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[4] A. Windaus, *Annalen*, 1927, **453**, 101.

[5] R. E. Marker, T. S. Oakwood, and H. M. Crooks, *J. Amer. Chem. Soc.*, 1936, **58**, 481; R. E. Marker, O. Kamm, T. S. Oakwood, and J. F. Laucius, *ibid.*, p. 1948.

[6] *J.*, 1936, 907.

by ethers of *epi*cholesterol, but not of cholesterol. The methyl, ethyl, and benzyl ethers of *epi*cholesterol (II) underwent replacement of their alkoxy-group by halogen under the influence of halogen acids or bromine at room temperature. In the latter case, of course, addition to the double bond also occurred. The hydroxyl group of neoergosterol (XIII) is also very labile.[7]

The capacity of a sterol derivative to form an insoluble compound with digitonin is determined by the *cis*-configuration of the hydroxyl group at C_3 with respect to the methyl group at C_{10} (see numbering given in formula I).* There are scarcely any exceptions to the generalisation that compounds which have this *cis*-configuration give insoluble compounds, whereas the *trans*-compounds do not. This applies not only to the sterols with intact side chain, including the phytosterols, but also to derivatives with degraded side chains [8] and to the male hormone group. However, profound modification of the side chain may prevent the formation of an insoluble digitonide. T. Wagner-Jauregg and L. Werner [9] showed that "β-cholesterol," which arises by the reduction of cholestenone with sodium and alcohol, is a molecular compound of cholestanol with a sterol which is not precipitated by digitonin. This second component has now been shown [10] to be *epiallo*cholesterol (IV).

Several investigations have been published dealing with brominated sterols and sterol-ketones.[11] One of the underlying objects was doubtless the chemical transformation of ring I of cholesterol to the aromatic state with a view to the conversion of

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[7] J. W. Cook and G. A. D. Haslewood, *Chem. and Ind.*, 1934, **53**, 507; K. Bonstedt, *Z. physiol. Chem.*, 1929, **185**, 165.

[8] E. Fernholz, *Z. physiol. Chem.*, 1935, **232**, 97; F. Reindel and K. Niederländer, *Annalen*, 1936, **522**, 218.

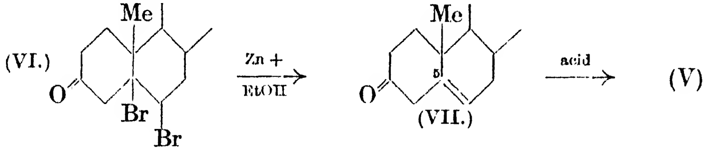
[9] *Z. physiol. Chem.*, 1932, **208**, 72.

[10] E. A. Evans and R. Schoenheimer, *J. Biol. Chem.*, 1936, **115**, 17.

[11] H. H. Inhoffen, *Ber.*, 1936, **69**, 1134, 1702, 2141; Y. Urushibara and T. Ando, *Bull. Chem. Soc. Japan*, 1936, **11**, 434; A. Butenandt and G. Schramm, *Ber.*, 1936, **69**, 2289; A. Butenandt, G. Schramm, A. Wolff, and H. Kudszus, *ibid.*, p. 2779; L. Ruzicka, W. Bosshard, W. H. Fischer, and H. Wirz, *Helv. Chim. Acta*, 1936, **19**, 1147; E. Dane, Y. Wang, and W. Schulte, *Z. physiol. Chem.*, 1936, **245**, 80.

* *Note on Nomenclature.* R. Schoenheimer and E. A. Evans (*J. Biol. Chem.*, 1936, **114**, 567) have commented on the difficulty introduced by the nomenclature proposed by L. Ruzicka, H. Brüngger, E. Eichenberger, and J. Meyer (*Helv. Chim. Acta*, 1934, **17**, 1407) whereby the configuration of the hydroxyl group is defined with respect to a hydrogen atom at C_5, which is of variable configuration and in many cases is non-existent. Schoenheimer and Evans suggest that the methyl group at C_{10} furnishes a more suitable standard of reference. This convention has been adopted in the present Report, with the reservation that the absolute configurations assigned to the hydroxyl group at C_3 still require proof.

this sterol into oestrone. So far this object has not been achieved. A convenient method for the preparation of Δ^4-cholestenone (V) has been described by R. Schoenheimer,[12] who used sodium iodide for the debromination of the ketone (VI) formed by oxidation of cholesterol dibromide. By this method, as with zinc and acetic acid,[13] debromination is accompanied by migration of the double bond. By carrying out the debromination in neutral solution with zinc and an alcohol, A. Butenandt and J. Schmidt-Thomé [14] have shown that migration does not occur, Δ^5-cholestenone (VII) being obtained from (VI). By brief warming with dilute acid the Δ^5-compound is rearranged to the Δ^4-ketone.



This observation has been utilised in the preparation of Δ^5-pregnene-3 : 20-dione,[15] isomeric with the hormone of the corpus luteum, and Δ^5-androsten-17-ol-3-one,[16] isomeric with the male hormone testosterone (p. 358). The high degree of structural specificity of the corpus luteum hormone is illustrated by the fact that Δ^5-pregnenedione showed no indication of physiological activity in the doses employed (0·6 and 2·0 mg.). Evidently the organism is unable to transform the Δ^5-compound into progesterone * (Δ^4-pregnenedione), although the transformation is readily effected by dilute mineral acid, even in the cold. The new isomeride of testosterone is 2½ times less active than the hormone.

The stereochemical configuration of the molecule with respect to the junction of rings I and II (*i.e.*, of the hydrogen atom at C_5) has been shown to have a marked influence on the position of bromination of ketones related to the sterols.[17] Compounds of the

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[12] *J. Biol. Chem.*, 1935, **110**, 461.

[13] See, for example, L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1935, **18**, 986.

[14] *Ber.*, 1936, **69**, 882.

[15] U. Westphal and J. Schmidt-Thomé, *Ber.*, 1936, **69**, 889.

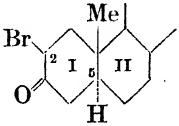
[16] A. Butenandt and G. Hanisch, *ibid.*, p. 2773.

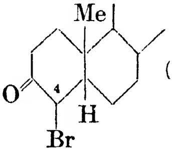
[17] A. Butenandt and J. Schmidt, *Ber.*, 1934, **67**, 1901; A. Butenandt and L. Mamoli, *Ber.*, 1935, **68**, 1850, 1854; A. Butenandt and A. Wolff, *ibid.*, p. 2091; A. Butenandt and H. Dannenberg, *Ber.*, 1936, **69**, 1158.

* Workers in the field have agreed to adopt this name for the pure crystalline hormone of the corpus luteum (progestin, luteosterone). The polymorphic forms, m. p. 128° and 121°, are termed α- and β-progesterone, respectively (W. M. Allen, A. Butenandt, G. W. Corner, and K. H. Slotta, *Nature*, 1935, **136**, 303).

trans-series (cholestanone, 3-ketobis*norallo*cholanic acid, *allo*pregnanedione, androstanedione) give 2-bromo-compounds (VIII), whereas the corresponding *cis*-compounds (coprostanone, 3-keto-bis*nor*cholanic acid, pregnanedione) give 4-bromo-derivatives (IX).

(VIII.)

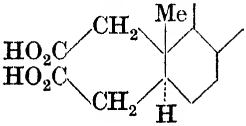


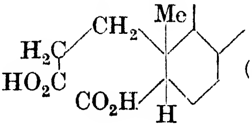


(IX.)

Analogous behaviour is shown in the oxidation of such ketones, for coprosterol and the bile acids (*cis*-series) give mainly bilianic acids (XI), whereas cholestanol (*trans*-series) gives, by opening of ring I and degradation of the side chain, *iso*lithobilianic acid (X).[18]

(X.)





(XI.)

The difference in reactivity between the ketones of the two stereoisomeric series is doubtless determined by a tendency for the enolic double bond to take up the 2 : 3-position in the *trans*-series and the 3 : 4-position in the *cis*-series.

The correspondence in structure and configuration between cholesterol and its homologue sitosterol, $C_{29}H_{50}O$, has been established by degradation of dihydrositosterol to the same 3-hydroxy-17-ætio*allo*cholanone obtained from dihydrocholesterol.[19] The same ketone has been obtained from the dihydro-derivative of cinchol, the sterol of cinchona bark.[20] Evidence is also forthcoming that sitostanol (both natural sterol and dihydrositosterol) is identical with stigmastanol [21] and also with fucostanol [22] and oestreastanol.[23] Furthermore α-dihydrofucosterol appears to be identical with the sitosterol of wheat germ oil, with a double bond at positions 5 : 6.[22] Fucosterol differs from the isomeric stigmasterol in the position of the second double bond, which is in the side chain ($\Delta^{22:23}$) [24] of stigmasterol, and in the nucleus of fucosterol.[25] Thus there is a

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[18] H. Wieland, E. Dane, and C. Martius, *Z. physiol. Chem.*, 1933, **215**, 18; R. Langer, *ibid.*, 1933, **216**, 189.

[19] L. Ruzicka and E. Eichenberger, *Helv. Chim. Acta*, 1935, **18**, 430.

[20] W. Dirscherl, *Z. physiol. Chem.*, 1935, **235**, 1.

[21] B. E. Bengtsson, *ibid.*, 1935, **237**, 46.

[22] D. H. Coffey, I. M. Heilbron, and F. S. Spring, *J.*, 1936, 738.

[23] W. Bergmann, *J. Biol. Chem.*, 1934, **104**, 317, 553.

[24] A. Guiteras, *Z. physiol. Chem.*, 1933, **214**, 89.

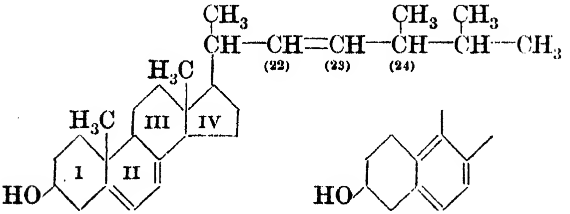
[25] I. Heilbron, R. F. Phipers, and H. R. Wright, *J.*, 1934, 1572.

surprisingly close structural relationship between the characteristic sterols of molluscs (oestreasterol [23]), algae (fucosterol), and the plant sterols (stigmasterol, sitosterol, sitostanol). These all differ from cholesterol (I) by the presence of an ethyl group at C_{24} of the side chain.

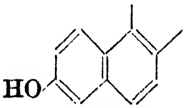
Lanosterol, the chief constituent of the "*iso*cholesterol" of wool-fat,[26] appears to belong to the group of triterpene resin alcohols, as its selenium dehydrogenation gives 1 : 2 : 8-trimethylphenanthrene, and not 3′-methyl-1 : 2-*cyclo*pentenophenanthrene.[27]

The hypothesis that vitamin E, the vitamin necessary for fertility in animals, is related to the phytosterols is supported by the isolation from wheat germ oil of an alcohol, $C_{29}H_{50}O_2$, which has the physiological activity of the vitamin.[28] This alcohol was not obtained crystalline, but was characterised by its crystalline allophanate and *p*-nitrophenylurethane; the alcohol shows selective absorption with a maximum at 2980 A., and a secondary band, slightly less intense, at 2920 A. It is doubtless the compound present in a highly active concentrate obtained by J. C. Drummond, E. Singer, and R. J. Macwalter,[29] who found that neither the biological activity nor the selective absorption is influenced by hydrogenation.

Ergosterol.—The structure (XII) of this important sterol has now been completely elucidated. The evidence for the nature of the side chain and the ring system, and for the position of the hydroxyl group has been reviewed already.[30] The location of the nuclear double bonds in ring II was established by H. Honigmann's [31] dehydrogenation of neoergosterol (XIII) [32] to a phenol (XIV) containing a naphthalene system. This shows that ring II and not



(XII.) (XIII.)



(XIV.)

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[26] Compare A. Windaus and R. Tschesche, *Z. physiol. Chem.*, 1930, **190**, 51.

[27] H. Schulze, *ibid.*, 1936, **238**, 35; see also C. Dorée and V. A. Petrow, *J.*, 1936, 1562.

[28] H. M. Evans, O. H. Emerson, and G. A. Emerson, *J. Biol. Chem.*, 1936, **113**, 319.

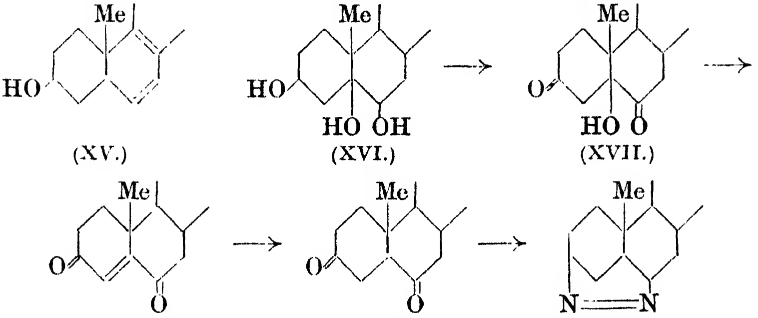
[29] *Biochem. J.*, 1935, **29**, 456.

[30] *Ann. Reports*, 1933, **30**, 210; 1934, **31**, 211.

[31] *Annalen*, 1934, **511**, 292.

[32] H. H. Inhoffen, *ibid.*, 1932, **497**, 130.

ring III is the aromatic ring of neoergosterol, and hence contains the nuclear double bonds of ergosterol, a conclusion which is supported by the spectroscopic examination of three hydrocarbons related to neoergosterol.[33] The chemical properties of ergosterol and its ultra-violet absorption[34] require that the nuclear double bonds should be conjugated, so the choice of structures becomes limited to (XII) and (XV). The decision in favour of (XII) was made by A. Windaus, H. H. Inhoffen, and S. v. Reichel,[35] who showed that treatment of ergosterol with perbenzoic acid, followed by hydrolysis, gives an ergostadienetriol which is hydrogenated to the ergostanetriol (XVI) of I. M. Heilbron, A. L. Morrison, and J. C. E. Simpson.[36] This triol is oxidised to a hydroxy-diketone (XVII), which is dehydrated to ergostenedione (XVIII) and this is



(XV.) (XVI.) (XVII.)

(XVIII.) (XIX.) (XX.)

reduced to ergostane-3 : 6-dione (XIX), the constitution of which follows from its reaction with hydrazine to give a pyridazine derivative (XX). These transformations of ergostanetriol (XVI) are exactly parallel to those effected with cholestane-3 : 5 : 6-triol,[37] of which the constitution is certain, and there is complete correspondence in chemical properties between the intermediate products in the two series. A similar method had already been used to establish the position of the 5 : 6-double bond of stigmasterol.[38] The 5 : 6-position of one of the double bonds of ergosterol was shown independently by J. L. Dunn, I. M. Heilbron, R. F. Phipers, K. M. Samant, and F. S. Spring.[39]

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[33] G. A. D. Haslewood and (Miss) E. Roe, *J.*, 1935, 465.

[34] Compare K. Dimroth and G. Trautmann, *Ber.*, 1936, **69**, 669.

[35] *Annalen*, 1934, **510**, 248.

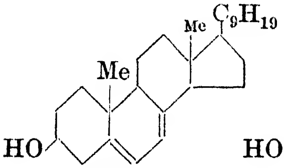
[36] *J.*, 1933, 302.

[37] A. Windaus, *Ber.*, 1907, **40**, 257; R. H. Pickard and J. Yates, *J.*, 1908, **93**, 1679; T. Westphalen, *Ber.*, 1915, **48**, 1064; A. Windaus and E. Kirchner, *Ber.*, 1920, **53**, 614.

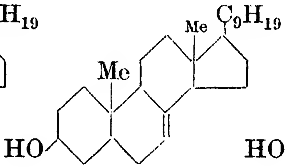
[38] *Ann. Reports*, 1934, **31**, 210.

[39] *J.*, 1934, 1576.

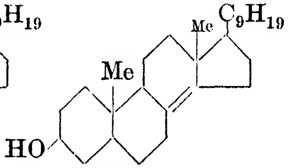
The reduction of the double bond in the side chain of ergosterol without disturbance of the nuclear system was accomplished in an elegant manner by A. Windaus and R. Langer.[40] The adduct of ergosteryl acetate and maleic anhydride was reduced to the dihydro-compound,[41] which underwent thermal dissociation to give the acetate of 22-dihydroergosterol (XXI). Reduction of (XXI) with sodium and alcohol gives γ-ergostenol (XXII), which is isomerised by a palladium or platinum catalyst to the well-known α-ergostenol, containing an "inert" double bond.[42] Formula (XXIII) is now favoured for α-ergostenol[43] and on the basis of selenium dioxide oxidation experiments R. K. Callow[44] has derived an analogous structure for the stereoisomeric α- and β-*apo*cholic acids.



(XXI.)

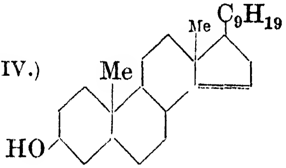


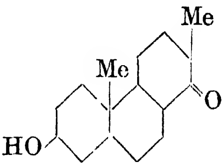
(XXII.)



(XXIII.)

(XXIV.)





(XXV.)

β-Ergostenol, which arises by isomerisation of α-ergostenol with hydrochloric acid,[45] has now been shown to have the structure (XXIV). β-Ergostenyl acetate was ozonised, and the ozonide submitted to reductive fission, followed by thermal decomposition. In this way[46] opening of ring IV was followed by splitting off of the side chain as an unsaturated aldehyde, $C_{12}H_{22}O$, with the production of the acetate of a keto-alcohol, the structure of which (XXV) follows from its dehydrogenation with selenium to 2-methyl-phenanthrene.[43]

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[40] *Annalen*, 1934, **508**, 105.

[41] H. H. Inhoffen, *ibid.*, p. 81.

[42] Compare F. Reindel and E. Walter, *ibid.*, 1928, **460**, 214; S. v. Reichel, *Z. physiol. Chem.*, 1934, **226**, 146.

[43] F. Laucht, *ibid.*, 1935, **237**, 236.

[44] *J.*, 1936, 462; compare H. Wieland, E. Dietz, and H. Ottawa, *Z. physiol. Chem.*, 1936, **244**, 194.

[45] I. M. Heilbron and D. G. Wilkinson, *J.*, 1932, 1708; compare F. Reindel, E. Walter, and H. Rauch, *Annalen*, 1927, **452**, 34.

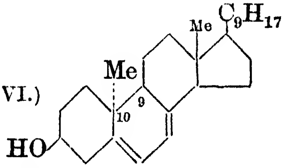
[46] Th. Achtermann, *Z. physiol. Chem.*, 1934, **225**, 141.

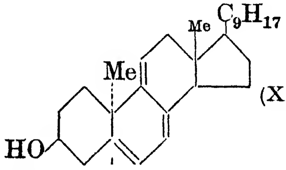
The Vitamin D Problem.

There have been developments of outstanding importance in this field, and although it is evident that the problem is more complex than was formerly suspected, we now have fairly precise knowledge of the chemistry of at least some of the natural antirachitic vitamins. The main outlines of the chemistry of the photoisomerides of ergosterol have been established; the structure of calciferol has been elucidated; new vitamins and provitamins have been prepared artificially from sterols, and the isolation of natural vitamins and provitamins has been accomplished.

Lumisterol, the first of the series of ultra-violet irradiation products of ergosterol, appears to be stereoisomeric with ergosterol.[47] It contains intact the tetracyclic sterol ring system, as it is dehydrogenated to 3′-methyl-1 : 2-*cyclo*pentenophenanthrene,[48] but unlike ergosterol it gives no insoluble precipitate with digitonin, although by epimerisation of their hydroxyl groups *iso*lumisterol, dihydrolumisterol, and lumistanol are converted into isomerides which are precipitated by digitonin.[49] Dehydrolumisterol, obtained by mild dehydrogenation of lumisterol with mercuric acetate,[47] was shown by K. Dimroth [50] to give a perhydro-derivative which differs from lumistanol and also from ergostanol, but is identical with perhydropyrocalciferol (p. 351). If dehydrolumisterol (like dehydroergosterol) is correctly represented by formula (XXVII), the difference between these two perhydro-compounds lies solely in the configuration of C_9, and the experimental results are consistent with Dimroth's conclusion that the conversion of ergosterol into lumisterol (XXVI) consists solely in the inversion of configuration of C_{10}.

(XXVI.)





(XXVII.)

H. Lettré's [51] observation that calciferol (vitamin D_2) gives no 3′-methyl-1 : 2-*cyclo*pentenophenanthrene when dehydrogenated with selenium led him to a further study of tachysterol, which is intermediate between lumisterol and calciferol in the series of irradiation products of ergosterol. This was shown to contain not

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[47] I. M. Heilbron, F. S. Spring, and P. A. Stewart, *J.*, 1935, 1221.

[48] K. Dimroth, *Ber.*, 1935, **68**, 539.

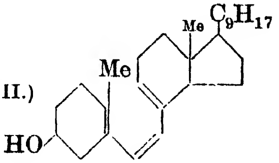
[49] A. Windaus, K. Dithmar, and E. Fernholz, *Annalen*, 1932, **493**, 259; G. Ahrens, E. Fernholz, and W. Stoll, *ibid.*, 1932, **500**, 109.

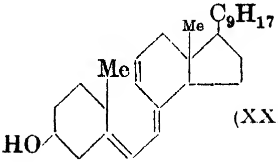
[50] *Ber.*, 1936, **69**, 1123.

[51] *Annalen*, 1934, **511**, 280.

three, but four double bonds (three of them conjugated). Hence tachysterol is tricyclic, which means that ring fission has occurred, and Lettré suggested that its structure is (XXVIII) or (XXIX).

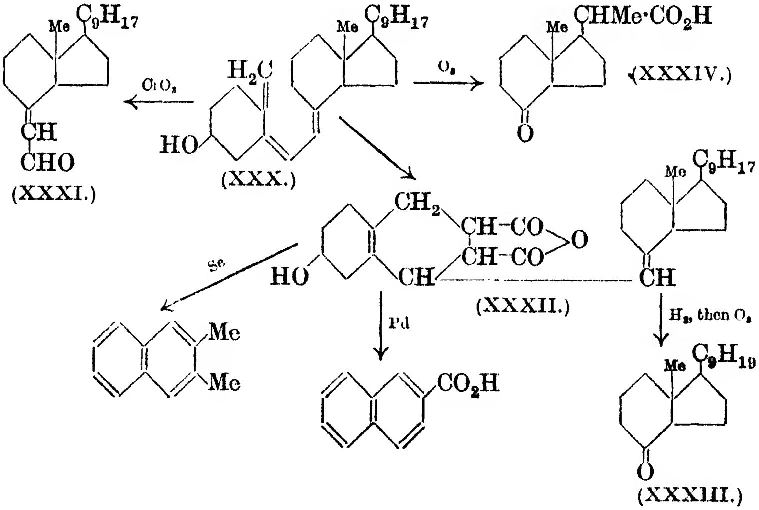
(XXVIII.)





(XXIX.)

The essential accuracy of this conception has been demonstrated by investigations which have established the structure (XXX) for calciferol (vitamin D_2), the succeeding member in the photochemical series. I. M. Heilbron, K. M. Samant, and F. S. Spring [52] obtained, by oxidation of calciferol with chromic acid, an unsaturated aldehyde $C_{21}H_{34}O$ (XXXI), the formation of which can only be interpreted by the assumption that fission of ring II has occurred in the conversion of ergosterol (XII) into calciferol. The location of the double bonds was elegantly shown by A. Windaus and W. Thiele,[53] who dehydrogenated the adduct of calciferol with maleic anhydride (XXXII), and obtained β-naphthoic acid with palladised charcoal, and 2 : 3-dimethylnaphthalene with selenium. Further, a saturated ketone, $C_{19}H_{34}O$ (XXXIII), was obtained by ozonisation of the dihydro-derivative of this maleic anhydride adduct :



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[52] *Nature*, 1935, **135**, 1072.

[53] *Annalen*, 1935, **521**, 160.

Finally, Heilbron and his collaborators[54] and A. Windaus and W. Grundmann[55] isolated a keto-acid, $C_{13}H_{20}O_3$ (XXXIV), from the products of direct ozonolysis of calciferol (XXX). The chemical evidence appears conclusive, although J. D. Bernal and D. Crowfoot[56] find difficulty in reconciling the *X*-ray crystallographic data with this formulation.

In connexion with these investigations the degree of unsaturation of calciferol and its derivatives has been re-examined. Although only three double bonds could be detected in calciferol by perbenzoic acid titration,[57] microhydrogenation has demonstrated[58] the presence of the four double bonds required by the tricyclic structure (XXX) of the vitamin. Furthermore, dihydrocalciferol,[59] which may also be obtained by reduction of tachysterol,[60] has been shown to contain three double bonds by perbenzoic acid titration[61] and by refractometric measurements.[60] In the thermal transformation of calciferol to pyrocalciferol and "*iso*pyrovitamin"[62, 63] the tetracyclic sterol system is re-formed (compare p. 349), 3′-methyl-1 : 2-*cyclo*pentenophenanthrene being formed by subsequent selenium dehydrogenation.[60] The epimerides of di- and hexahydropyrocalciferol are precipitated by digitonin.[63] Suprasterols I and II, which arise by further irradiation of calciferol, are also tetracyclic, but give no crystalline products on dehydrogenation.[60]

In the meantime, it became apparent on biological grounds that calciferol is not the only antirachitic vitamin. For instance, J. Waddell[64] showed that irradiated cholesterol and cod-liver oil are more effective in curing rachitic chicks than irradiated ergosterol, compared on the basis of the same number of rat units.[65]

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[54] I. M. Heilbron, R. N. Jones, K. M. Samant, and F. S. Spring, *J.*, 1936, 905.

[55] *Annalen*, 1936, **524**, 295.

[56] *Chem. and Ind.*, 1935, **54**, 701.

[57] A. Windaus, O. Linsert, A. Lüttringhaus, and G. Weidlich, *Annalen*, 1932, **492**, 226.

[58] R. Kuhn and E. F. Möller, *Angew. Chem.*, 1934, **47**, 145.

[59] E. Fernholz, *Annalen*, 1932, **499**, 198.

[60] M. Müller, *Z. physiol. Chem.*, 1935, **233**, 223.

[61] S. v. Reichel and M. Deppe, *ibid.*, 1936, **239**, 143.

[62] F. A. Askew, R. B. Bourdillon, H. M. Bruce, R. K. Callow, J. St. L. Philpot, and T. A. Webster, *Proc. Roy. Soc.*, 1932, *B*, **109**, 488.

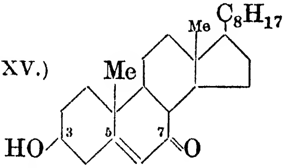
[63] P. Busse, *Z. physiol. Chem.*, 1933, **214**, 211.

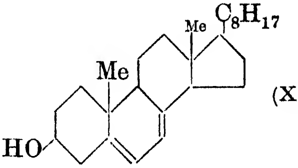
[64] *J. Biol. Chem.*, 1934, **105**, 711; for a discussion of "The Multiple Nature of Vitamin D" see C. E. Bills, Cold Spring Harbor Symposia on Quantitative Biology, 1935, **3**, 328.

[65] See also O. N. Massengale and M. Nussmeier, *J. Biol. Chem.*, 1930, **87**, 415, 423; A. F. Hess and G. C. Supplee, *Proc. Soc. Exp. Biol. Med.*, 1930, **27**, 609; M. J. L. Dols, *Z. Vitaminforsch.*, 1936, **5**, 161; A. Black and H. L. Sassaman, *Amer. J. Pharm.*, 1936, **108**, 237.

The double bond in the side chain of calciferol is evidently not essential for activity, for 22-dihydroergosterol (p. 348) acquires antirachitic properties on irradiation.[40] This led to the suggestion [66] that the analogous derivative of cholesterol, without the additional methyl group of the side chain, might be the provitamin normally present in cholesterol. This compound (XXXVI), for which the term 7-dehydrocholesterol was suggested by C. E. Bills,[64] was prepared from cholesterol by A. Windaus, H. Lettré, and Fr. Schenk [67] by oxidation of cholesteryl acetate to the 7-keto-compound (XXXV), followed by reduction with aluminium *iso*propoxide, and pyrolysis of the dibenzoate of the resulting Δ^5-cholestene-3 : 7-diol.

(XXXV.)





(XXXVI.)

In a similar manner sitosterol [68] and stigmasterol [69] have been converted into 7-dehydro-derivatives. In its absorption spectrum,[67] its photochemical oxidation and dehydrogenation, and its conversion into a series of dihydro-compounds, γ-, α-, and β-cholestenols,[70] 7-dehydrocholesterol shows a very close resemblance to ergosterol and 22-dihydroergosterol, and it acquires powerful antirachitic properties on irradiation. The vitamin so formed has been isolated in the pure state by A. Windaus, Fr. Schenk, and F. v. Werder [71] and has been termed vitamin D_3. Moreover, the irradiation products of both 22-dihydroergosterol and 7-dehydrocholesterol are just as effective in curing rachitic chickens, on the basis of the number of rat units which they contain, as the vitamin D of cod-liver oil and irradiated crude cholesterol.[72] Irradiated 7-dehydrositosterol has antirachitic properties, but is less active than irradiated ergosterol, and it is remarkable that the antirachitic activity of irradiated 7-dehydrostigmasterol is either feeble or nil; for this sterol differs from ergosterol only by the presence of an additional methyl group in the side chain.

The isolation from natural sources of the provitamin 7-dehydrocholesterol (XXXVI), and also its irradiation product vitamin D_3,

[66] R. K. Callow, *Sci. J. Roy. Coll. Science*, 1934, **4**, 41.

[67] *Annalen*, 1935, **520**, 98.

[68] W. Wunderlich, *Z. physiol. Chem.*, 1936, **241**, 116.

[69] O. Linsert, *ibid.*, p. 125.

[70] Fr. Schenk, K. Buchholz, and O. Wiese, *Ber.*, 1936, **69**, 2696.

[71] *Z. physiol. Chem.*, 1936, **241**, 100.

[72] W. Grab, *ibid.*, 1936, **243**, 84.

has now been achieved. Using the method of chromatographic adsorption on alumina and working with a cholesterol of unspecified origin, containing as much as 4·5% of provitamin D, estimated from the intensity of its characteristic ultra-violet absorption, A. G. Boer, E. H. Reerink, A. van Wijk, and J. van Niekerk [73] isolated pure 7-dehydrocholesterol. Actiniasterol, a sterol isolated in the previous year by E. Klenk and W. Diebold [74] from the fat of the sea anemone, shows very close resemblance in its recorded properties to 7-dehydrocholesterol, except that the optical rotations, measured in different solvents, show considerable divergence. Vitamin D_3, which has almost the same absorption spectrum as calciferol (XXX) and presumably has an analogous structure, was isolated from tunny-liver oil by H. Brockmann.[75] This is clearly not the only natural vitamin, however, as A. Windaus and O. Stange [76] have now isolated ergosterol from cholesterol prepared from egg-yolk, although these authors point out that ergosterol is not necessarily synthesised by the hen, as there is evidence,[77] which they could corroborate, that ergosterol, fed to hens in small quantities, is gradually absorbed and appears again in the eggs. There is evidence of the existence of other antirachitic vitamins of a type chemically distinct from calciferol and vitamin D_3.[78]

Bile Acids.

The stereochemical relationships of the bile acids have been to some extent elucidated. Both lithocholic acid [79] and hyodeoxycholic acid [80] have been shown to belong to the *epi*coprosterol series (hydroxy-group at C_3 in the *trans*-position with respect to the methyl group at C_{10}; *cis*-fusion of rings I and II). Presumably this is also true of the other bile acids. By analogy with the varying capacities of lactonisation shown by stereoisomeric hydroxy*cyclo*hexanecarboxylic acids H. Lettré [81] concluded that the hydroxyl group at C_7 of cholic and chenodeoxycholic (= anthropodeoxycholic) acids is in the *trans*-position to the methyl group at C_{10}. The validity of this

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[73] *Proc. K. Akad. Wetensch. Amsterdam*, 1936, **39**, 622.

[74] *Z. physiol. Chem.*, 1935, **236**, 141.

[75] *Ibid.*, 1936, **241**, 104; see also E. J. H. Simons and T. F. Zucker, *J. Amer. Chem. Soc.*, 1936, **58**, 2655.

[76] *Z. physiol. Chem.*, 1936, **244**, 218.

[77] R. Schoenheimer and H. Dam, *ibid.*, 1932, **211**, 241; W. Menschick and I. H. Page, *ibid.*, p. 246.

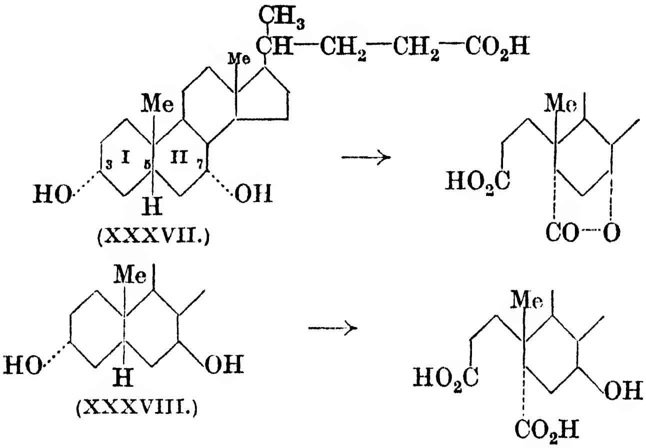
[78] O. Rygh, *Nature*, 1935, **136**, 552.

[79] L. Ruzicka and M. W. Goldberg, *Helv. Chim. Acta*, 1935, **18**, 668.

[80] O. Dalmer, F. v. Werder, H. Honigmann, and K. Heyns, *Ber.*, 1935, **68**, 1814.

[81] *Ibid.*, p. 766.

argument is supported by recent work on ursodeoxycholic acid, which is shown to be stereoisomeric with chenodeoxycholic acid, differing from it in the configuration of the hydroxyl group at C_7.[82] Hypobromite oxidation of chenodeoxycholic acid (XXXVII) gives a hydroxy-tricarboxylic acid which readily passes into a lactonic acid,[83] but the hydroxy-tricarboxylic acid similarly formed from ursodeoxycholic acid (XXXVIII) shows no tendency to lactonise [82]:



(XXXVII.)

(XXXVIII.)

The isolation of new bile acids has been recorded,[84] and by a convenient new method F. Cortese and L. Bauman [85] have prepared the naturally occurring conjugated bile acids, glycocholic and glycodeoxycholic acids. Recognition that the hydroxyl group at C_3 of the bile acids has the opposite configuration from that in the sterols has led to speculation concerning the possible mode of biological conversion of cholesterol into the bile acids. The fact that cholestenone is hydrogenated to coprostanone and then, in neutral solution, to *epi*coprosterol [86] supports the view that these ketones, which have not been isolated from natural sources, are concerned in cholesterol metabolism.[87] In attempting to secure evidence on this point R. Schoenheimer and his collaborators have adopted the interesting device of "labelling" the molecule by introducing deuterium. Cholestenone (V) was reduced with deuterium, and

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[82] T. Iwasaki, *Z. physiol. Chem.*, 1936, **244**, 181.

[83] A. Windaus and A. van Schoor, *ibid.*, 1926, **157**, 181.

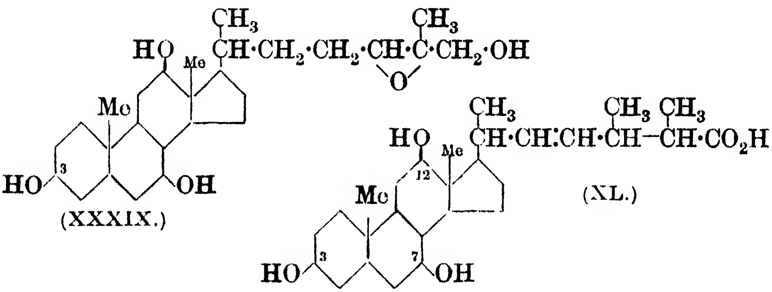
[84] H. Wieland and S. Kishi, *ibid.*, 1933, **214**, 47; W. Gumlich, *ibid.*, 1933, **215**, 18; E. Fernholz, *ibid.*, 1935, **232**, 202; S. Kishi, *ibid.*, 1936, **238**, 210.

[85] *J. Amer. Chem. Soc.*, 1935, **57**, 1393; *J. Biol. Chem.*, 1936, **113**, 779.

[86] L. Ruzicka, H. Brüngger, E. Eichenberger, and J. Meyer, *Helv. Chim. Acta*, 1934, **17**, 1407.

[87] Compare O. Rosenheim and T. A. Webster, *Nature*, 1935, **136**, 474.

when the resulting coprostanone-4 : 5-d_2 was fed to animals they excreted coprosterol containing deuterium,[88] in confirmation of the view that cholestenone and coprostanone are intermediates in the transformation of cholesterol into coprosterol. However, when the same coprostanone-4 : 5-d_2 was injected into dogs with bile fistulas, the cholic acid subsequently recovered from the bile contained no deuterium, so coprostanone had passed through the liver without the formation of cholic acid.[89] Naturally, this negative evidence does not prove that the bile acids are *not* formed in the body from cholesterol, with oxidative removal of three carbon atoms from the side chain. Of interest in this connexion is scymnol, present in the bile of sharks, for which formula (XXXIX) is probable.[90] If the hydroxyl group at C_3 is correctly placed, a point which has not been established with certainty, this alcohol would appear to represent an arrested stage in the transition from cholesterol to the bile acids. A compound of somewhat similar type, containing an oxidised ergosterol side chain, is trihydroxybufosterocholenic acid (XL) isolated from the winter bile of toads; this acid was ozonised



(XXXIX.)

(XL.)

to 3 : 7 : 12-trihydroxybis*nor*cholanic acid,[91] which was also obtained by "Wieland degradation" of cholic acid. H. Wieland and G. Hanke[92] have commenced a study of the weak acids of ox-bile and have isolated an acid of the probable formula $C_{29}H_{46}O_3$, which they term sapocholic acid. The properties of this interesting acid are very similar to those of pyroquinovaic acid,[93] particularly in respect to the reaction with bromine, which is characteristic of the

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[88] R. Schoenheimer, D. Rittenberg, and M. Graff, *J. Biol. Chem.*, 1935, **111**, 183.

[89] R. Schoenheimer, D. Rittenberg, B. N. Berg, and L. Rousselot, *ibid.*, 1936, **115**, 635.

[90] A. Windaus, W. Bergmann, and G. König, *Z. physiol. Chem.*, 1930, **189**, 148; R. Tschesche, *ibid.*, 1931, **203**, 263.

[91] T. Shimiza and T. Oda, *ibid.*, 1934, **227**, 74; T. Shimiza and T. Kazuno, *ibid.*, 1936, **244**, 167.

[92] *Ibid.*, 1936, **241**, 93.

[93] H. Wieland, A. Hartmann, and H. Dietrich, *Annalen*, 1936, **522**, 191.

triterpene sapogenins such as hederagenin and oleanolic acid. It may be that the triterpenes have a closer structural and biogenetic relationship to the sterol group than has hitherto been demonstrated.

Sex Hormones.

It is now recognised that the terms " male and female hormones " are unfortunate, as both groups of hormones are present in both sexes, and the biological effects of a hormone are not restricted to the reproductive organs of one sex. Moreover, the same compound may give rise to the characteristic biological effects of both male and female hormones. In general, however, the male hormones are understood to be those compounds of which the essential function is to promote growth of the secondary male organs, *e.g.*, the comb in the capon or the seminal vesicles of castrated male rats, and the female hormones are those which are highly potent in promoting the normal activities of the female reproductive organs, *e.g.*, oestrus and uterine enlargement in rodents. An extraordinarily large number of physiologically active compounds have been prepared by the methods made available by the work of Ruzicka,[94] and many interesting studies have been made of the effect of changes of structure and configuration on the biological activity.[95] The results here reported must be restricted largely to an outline of the structural features of the natural hormones.

The oxidation of *epi*cholestanol to androsterone was followed by the oxidation of sitosterol,[96] cholesterol,[97, 3] and stigmasterol [98, 3] to the dehydroandrosterone which Butenandt [99] had isolated from male urine. During oxidation of the sterols the hydroxyl group was protected by acetylation, and the double bond by addition of bromine. These degradations showed that dehydroandrosterone (XLI), unlike androsterone, has the *cis*-configuration of the hydroxyl group with respect to the methyl at C_{10}, a conclusion already drawn by W. Schoeller, A. Serini, and M. Gehrke [1] from the fact that dehydroandrosterone, but not androsterone, gives an insoluble compound with digitonin. Hence androsterone cannot be formed in the body by direct reduction of dehydroandrosterone. *epi*Dehy-

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[94] *Ann. Reports*, 1934, **31**, 207.

[95] See, for example, E. Tschopp, *Arch. internat. Pharm. Thérap.*, 1936, **52**, 381; R. Deanesly and A. S. Parkes, *Biochem. J.*, 1936, **30**, 291.

[96] R. V. Oppenauer, *Nature*, 1935, **135**, 1039.

[97] L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1935, **18**, 986; E. S. Wallis and E. Fernholz, *J. Amer. Chem. Soc.*, 1935, **57**, 1379, 1504; I. A. Remesov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **1**, 261.

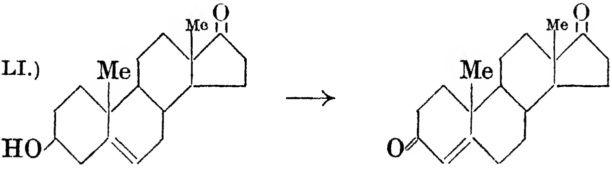
[98] L. Ruzicka, W. Fischer, and J. Meyer, *Helv. Chim. Acta*, 1935, **18**, 1483.

[99] A. Butenandt and H. Dannenbaum, *Z. physiol. Chem.*, 1934, **229**, 192.

[1] *Naturwiss.*, 1935, **23**, 337.

droandrosterone has recently been obtained by L. Ruzicka and M. W. Goldberg[2] as a product of partial hydrogenation with a nickel catalyst of Δ^5-androstenedione (compare formula VII).

(XLI.)



(XLII.)

The unsaturated chloro-ketone which is formed from dehydroandrosterone by the action of hydrochloric acid used in the course of isolation[99, 3] has also been prepared from cholesteryl chloride[4] and directly from dehydroandrosterone.[5]

Certain biological and chemical discrepancies rendered it unlikely that the hormone present in testicular extracts was either androsterone or dehydroandrosterone. The biological evidence depended upon differences of activity towards capons and rats[6] and was of a similar nature to that which led to the conclusion that calciferol was not the vitamin D of irradiated crude cholesterol (p. 351). Moreover, T. F. Gallagher and F. C. Koch[7] showed that the active principle of the testis is destroyed by boiling alkali. This suggested an αβ-unsaturated ketone and led to the preparation of androstene-3 : 17-dione (XLII),[8] which had the expected high activity in rats. When, shortly afterwards, the testicular hormone (testosterone) was isolated in the crystalline state and shown not to be androstenedione,[9] the alternative structure of Δ^4-androsten-17-ol-3-one (XLIV) came into consideration; it was known already that reduction of the 17-keto-group of androsterone results in a three-fold increase in biological activity.[10] This structure was rapidly confirmed by the

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[2] *Helv. Chim. Acta*, 1936, **19**, 1407.

[3] A. Butenandt, H. Dannenbaum, G. Hanisch, and H. Kudszus, *Z. physiol. Chem.*, 1935, **237**, 57.

[4] R. E. Marker, F. C. Whitmore, O. Kamm, T. S. Oakwood, and J. M. Blatterman, *J. Amer. Chem. Soc.*, 1936, **58**, 338.

[5] A. Butenandt and W. Grosse, *Ber.*, 1936, **69**, 2776.

[6] See, for example, E. Dingemanse, J. Freud, and E. Laqueur, *Nature*, 1935, **135**, 184.

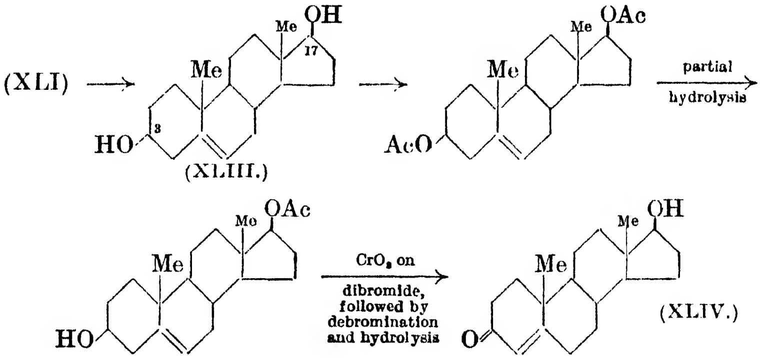
[7] *Endocrinology*, 1934, **18**, 107; *J. Biol. Chem.*, 1934, **104**, 611.

[8] L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1935, **18**, 986; A. Butenandt and G. Hanisch, *Ber.*, 1935, **68**, 1859; E. S. Wallis and E. Fernholz, *J. Amer. Chem. Soc.*, 1935, **57**, 1511.

[9] K. David, E. Dingemanse, J. Freud, and E. Laqueur, *Z. physiol. Chem.*, 1935, **233**, 281.

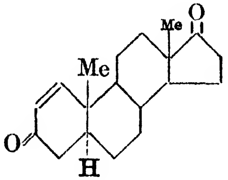
[10] L. Ruzicka, M. W. Goldberg, and J. Meyer, *Helv. Chim. Acta*, 1935, **18**, 210.

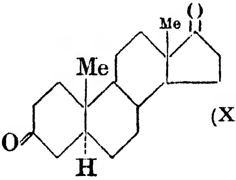
oxidation of testosterone to androstene-3 : 17-dione (XLII)[11] and by the preparation of testosterone from dehydroandrosterone, in accordance with the following scheme[12]:



The yields were subsequently much improved by the use of mixed esters of Δ^5-androstene-3 : 17-diol (XLIII).[13] This diol was shown by A. Butenandt[14] to have pronounced oestrogenic activity as well as male-hormone action; thus a single molecule has two types of biological activity which are in some respects mutually antagonistic. Even more striking is the influence of the position of a double bond on the activity of androstenedione, for, whereas the Δ^4-compound (XLII) has powerful male-hormone activity but no oestrogenic activity, the isomeric Δ^1-compound (XLV) is fairly strongly oestrogenic but has no male hormone action.[15]

(XLV.)





(XLVI.)

A Ogata and S. Hirano[16] isolated from testicular extracts a crystalline male hormone which differs in its properties from testosterone. L. Ruzicka and A. Wettstein[12] have suggested that this

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[11] K. David, *Acta Brev. Néerl.*, 1935, **5**, 85.

[12] A. Butenandt and G. Hanisch, *Ber.*, 1935, **68**, 1859; L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1935, **18**, 1264.

[13] L. Ruzicka, A. Wettstein, and H. Kägi, *ibid.*, p. 1478.

[14] *Naturwiss.*, 1936, **24**, 15.

[15] A. Butenandt and H. Dannenberg, *Ber.*, 1936, **69**, 1158.

[16] *J. Pharm. Soc. Japan*, 1934, **54**, 199.

is androstane-3 : 17-dione (XLVI), which can be prepared by oxidation of androsterone.[10, 17]

The most active natural male hormone is testosterone (XLIV), which shows high activity both in capons and in rats. It was shown by Laqueur and his collaborators[9] that testosterone displays its maximum biological activity only in the presence of an "X-substance" present in testicular extracts, and consequent upon investigations in which it was shown that many fatty acids can replace this "X-substance"[18] it was shown that by esterification of testosterone its activity may be much enhanced and also considerably prolonged. This is especially so with the esters of the lower fatty acids and the most active of these esters is the propionate,[19] which is now available for clinical use under the name of "perandren." It is evident that the function of the fatty acid or the "X-substance" is to promote absorption of the testosterone, the optimum effect being shown by an ester of testosterone which is slowly hydrolysed with constant production of biologically effective quantities of the hormone. This view is confirmed by the observation that, although 17-methyltestosterone is highly active, its acetate, which contains a very difficultly hydrolysable tertiary ester group, is completely inactive.[20]

In attempts to isolate cortin, the hormone of the adrenal cortex necessary for the maintenance of life, E. C. Kendall, T. Reichstein, and O. Wintersteiner, and their respective associates[21] have isolated several crystalline compounds, some of which are apparently related to the pregnane (C_{21}) group of sterol derivatives. One of Reichstein's compounds, adrenosterone, was an αβ-unsaturated diketone, $C_{19}H_{24}O_3$ or $C_{19}H_{26}O_3$, having comb-growth promoting activity. Reichstein also showed that three of his other compounds could be degraded to the same saturated diketone, $C_{19}H_{26}O_3$ or $C_{19}H_{28}O_3$, which had strong male hormone action in the capon test. This diketone, for which a structure of type (XLVII) is suggested, was reduced to 17-androstanone (XLVIII) and androstane.

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[17] A. Butenandt and K. Tscherning, *Z. physiol. Chem.*, 1934, **229**, 185.

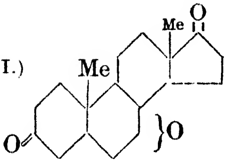
[18] K. Miescher, A. Wettstein, and E. Tschopp, *Schweiz. med. Woch.*, 1936, **66**, 310; *Biochem. J.*, 1936, **30**, 1970.

[19] L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1936, **19**, 1141; K. Miescher, A. Wettstein, and E. Tschopp, *Biochem. J.*, 1936, **30**, 1977; A. S. Parkes, *Lancet*, 1936, **231**, 674.

[20] Statement by Dr. K. Miescher at the meeting of the Biochemical Society on December 11th, 1936.

[21] H. L. Mason, C. S. Myers, and E. C. Kendall, *J. Biol. Chem.*, 1936, **114**, 613; **116**, 267; T. Reichstein, *Helv. Chim. Acta*, 1936, **19**, 29, 223, 402, 979, 1107; T. Reichstein and A. Goldschmidt, *ibid.*, p. 401; O. Wintersteiner and J. J. Pfiffner, *J. Biol. Chem.*, 1935, **111**, 599; 1936, **116**, 291.

(XLVII.)



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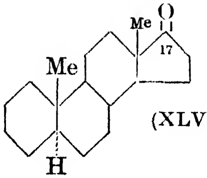

(XLVIII.)

A compound, $C_{21}H_{28}O_5$, isolated by both Kendall and Wintersteiner, was stated to have qualitatively the biological action of cortin by Kendall, who degraded it to a ketone, $C_{19}H_{24}O_3$, having male hormone activity. This and other observations support the view that cortin belongs to the pregnane–androstane group.* Of interest in this connexion is the isolation from the urine of a man with an adrenal tumour of relatively large amounts of an unsaturated ketone, $C_{19}H_{26}O$, which was hydrogenated to 17-androstanone (XLVIII).[22] The unsaturated ketone has since been shown (unpublished experiments) to be $\Delta^{3:5}$-androstadien-17-one. This compound could be formed, during the acid hydrolysis used in its isolation, by dehydration of *epi*dehydroandrosterone (compare p. 342).

In view of the confusion introduced into the earlier literature dealing with the oestrogenic hormones by the use of many names for the same substance it is satisfactory that the European representatives at the Second Conference on Standardisation of Sex Hormones agreed [23] to adopt the following nomenclature for these hormones : hydroxy-ketonic form = oestrone; trihydroxy-form = oestriol; dihydroxy-form = oestradiol. The structures of these hormones, and also of equilin and equilenin, have been established in every detail.[24] When, for instance, the methyl ether of oestradiol

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[22] H. Burrows, J. W. Cook, and F. L. Warren, *Chem. and Ind.*, 1936, **55**, 1031.

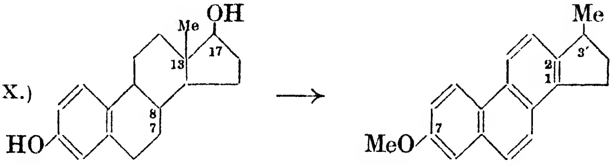
[23] *Quart. Bull. Hlth. Org., League of Nations*, 1935, **4**, 625; see also *J. Amer. Med. Assoc.*, 1936, **107**, 1221.

[24] A. Cohen, J. W. Cook, and C. L. Hewett, *J.*, 1935, 445; W. Dirscherl and F. Hanusch, *Z. physiol. Chem.*, 1935, **233**, 13; **236**, 131; J. W. Cook and E. Roe, *Chem. and Ind.*, 1935, **54**, 501.

* One of Reichstein's compounds (" substance H ") was stated to be an $\alpha\beta$-unsaturated ketone, $C_{19}H_{26}O_4$ or $C_{23}H_{32}O_5$ (*Helv. Chim. Acta*, 1936, **19**, 1107). This has now been freed from a small amount of higher-melting contaminant, and the pure ketone, m. p. 180—182°, was found to have in a very high degree the biological activity of the cortical hormone (P. de Fremery, E. Laqueur, T. Reichstein, R. W. Spanhoff, and I. E. Uyldert, *Nature*, 1937, **139**, 26). It is stated in this important paper that the constitution of the hormone has been elucidated except for a few details, and it is evident from the name, *corticosterone*, which these authors give to the compound, that they are satisfied that it is a ketone of the sterol group.

(XLIX) was dehydrated, and the product dehydrogenated, there was formed 7-methoxy-3′-methyl-1 : 2-*cyclo*pentenophenanthrene (L), identical with a synthetic specimen.

(XLIX.)

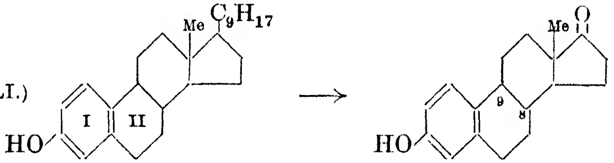


(L.)

By these and similar reactions in which dehydration of carbinols of type (XLIX) is accompanied by methyl migration it was shown that the carbonyl group of oestrone, equilin, and equilenin must be at C_{17}, and the quaternary methyl group at C_{13}. The other structural features had been proved already,[25] with the exception of the position of the ethylenic linkage of equilin, which is now placed at $C^{7:8}$ (compare formula XLIX).

The degradation of ergosterol (XII) to oestrone (LII) has been accomplished by R. E. Marker, O. Kamm, T. S. Oakwood, and J. F. Laucius,[26] who reduced Honigmann's dehydroneoergosterol (XIV) to a tetrahydro-compound (LI) in which the phenolic hydroxyl group is still present, so that, contrary to all analogies, ring II has been reduced.

(LI.)



(LII.)

Oestrone (LII) was isolated after oxidation of the acetate of (LI) with chromic acid. These reactions demonstrate only a partial stereochemical correspondence between the sterols and the oestrogenic hormones, for it is possible (though unlikely) that the configurations of the carbon atoms 8 and 9 of (LII) are different from those found in the original ergosterol.

Both stereoisomeric oestradiols (XLIX), m.p.'s 172° and 209°, which are formed by reduction of oestrone (LII),[27] have been isolated from mares' urine.[28] One of these (the principal reduction product,

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[25] *Ann. Reports*, 1934, **31**, 214.

[26] *J. Amer. Chem. Soc.*, 1936, **58**, 1503; see, however, A. Windaus and M. Deppe, *Ber.*, 1937, **70**, 76.

[27] E. Schwenk and F. Hildebrandt, *Naturwiss.*, 1933, **21**, 177.

[28] O. Wintersteiner, E. Schwenk, and B. Whitman, *Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 1087; see also O. Wintersteiner, E. Schwenk, H. Hirschmann, and B. Whitman, *J. Amer. Chem. Soc.*, 1936, **58**, 2652.

m.p. 172°) has been isolated from the *liquor folliculi* of sows' ovaries [29] and is evidently the true follicular hormone. Its oestrogenic activity is several times that of oestrone.

It is unlikely that the sex hormones are present in urine in the free state, and the water-soluble complex of oestriol has been isolated and shown to be probably a monoglucuronic acid [30]; the glucuronic acid of pregnandiol [31] has also been isolated from human pregnancy urine.[32]

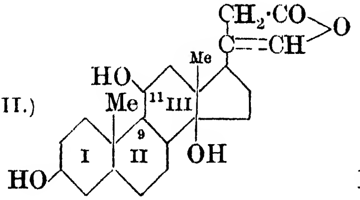
An unexpected development in the field of oestrogenic hormones was the isolation from ovarian tissue by R. H. Andrew and F. Fenger [33] of a crystalline nitrogenous compound which gave a delayed but prolonged oestrous response in rats in doses of 10^{-5} mg. (*i.e.*, about 1/50 of the dose of oestrone necessary for oestrogenic action). If the formula $C_{20}H_{41}O_2N$ suggested by analysis is correct, this compound cannot be a tetracyclic sterol derivative.

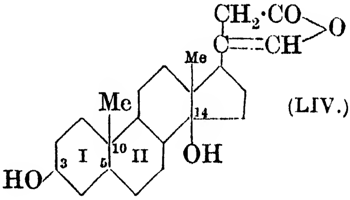
Cardiac Aglycones.

The chemistry of these substances was reviewed in these Reports in terms of the modern structures in 1934, and more recent work, mainly by R. Tschesche, has amply confirmed the main structural features, and has filled in many of the details.

Digoxigenin, a digitalis aglycone containing one tertiary and two secondary hydroxyl groups, has not been correlated with the other members of the group, but resembles digitoxigenin very closely. Structure (LIII) is favoured for digoxigenin, the secondary hydroxyl group being placed at C_{11} mainly because no other position can be readily reconciled with the chemical properties.[34]

(LIII.)





(LIV.)

R. Tschesche [35] has shown that thevetigenin differs from uzarigenin

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[29] D. W. MacCorquodale, S. A. Thayer, and E. A. Doisy, *Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 1182; *J. Biol. Chem.*, 1936, **115**, 435.

[30] S. L. Cohen and G. F. Marrian, *Biochem. J.*, 1936, **30**, 57; S. L. Cohen, G. F. Marrian, and A. D. Odell, *ibid.*, p. 2250.

[31] See *Ann. Reports*, 1931, **28**, 237.

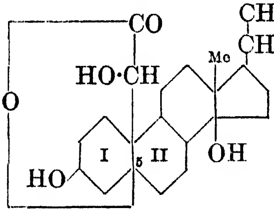
[32] E. M. Venning and J. S. L. Browne, *Proc. Soc. Exp. Biol. Med.*, 1936, **34**, 792.

[33] *Science*, 1936, **84**, 18; *Endrocrinology*, 1936, **20**, 563.

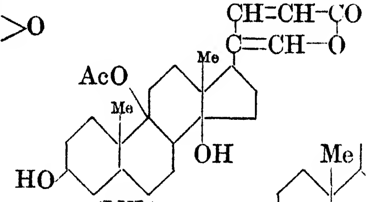
[34] S. Smith, *J.*, 1935, 1305; R. Tschesche and K. Bohle, *Ber.*, 1936, **69**, 793.

[35] *Ber.*, 1936, **69**, 2368.

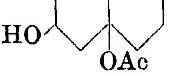
(LIV) only in the configuration of C_5; in thevetigenin there is a *cis*-fusion, and in uzarigenin a *trans*-fusion of rings I and II, and in both genins the hydroxyl group at C_3 occupies the *cis*-position with respect to the methyl at C_{10}. Digitoxigenin differs from them in the latter respect; the C_3 hydroxyl group is *trans* to the methyl at C_{10}, and there is a *cis*-locking of rings I and II. These stereochemical relationships suggested that the low biological activity of uzarin is due to the *trans*-fusion of rings I and II, and as W. A. Jacobs and R. C. Elderfield[36] had suggested a similar configuration for strophanthidine and probably also periplogenin, the latter question was reconsidered by R. Tschesche and K. Bohle.[37] By submitting dihydrostrophanthidine to the cyanohydrin synthesis, W. A. Jacobs and R. C. Elderfield[38] had obtained a hydroxy-acid which readily undergoes lactonisation involving the hydroxyl at C_5. Tschesche and Bohle infer from models that such a lactone (LV) can only be formed if there is a *cis*-fusion of rings I and II.



(LV.)



(LVI.)



(LVII.)

It is concluded that both strophanthidine and periplogenin have *cis*-fusions of rings I and II, and that this configuration is present in all the highly active heart poisons of the digitalis group.

Sarmentogenin,[39] a genin from the seeds of *Strophanthus sarmentosus*, and other species of *Strophanthus* which have not been identified with certainty, has been converted by R. Tschesche and K. Bohle[40] into a saturated lactone identical with that similarly obtained from digitoxigenin by A. Windaus and G. Stein.[41] As sarmentogenin gives no precipitate with digitonin, the hydroxyl group assumed to be at C_3 should be *trans* to the methyl group at C_{10}. The corresponding diketone, sarmentogenone, like digoxigenone, contains a non-reactive carbonyl group, which is likewise

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[36] *J. Biol. Chem.*, 1935, **108**, 506.

[37] *Ber.*, 1936, **69**, 2443.

[38] *J. Biol. Chem.*, 1936, **113**, 625.

[39] W. A. Jacobs and M. Heidelberger, *ibid.*, 1929, **81**, 765; R. Tschesche, *Ber.*, 1935, **68**, 423.

[40] *Ber.*, 1936, **69**, 2497.

[41] *Ber.*, 1928, **61**, 2436.

placed at C_{11}, and it is inferred that sarmentogenin is a stereoisomeride of digoxigenin (LIII), differing only in the configuration about C_9. It is considered likely that in digoxigenin the configuration of C_9 is that of the sterols, since the genins of the glycosides digitoxin and gitoxin, from the same plant, have this configuration, and that sarmentogenin has the opposite configuration. If this conception be correct, sarmentogenin is unique among the natural products related to the sterols, in that rings II and III would be locked in the *cis*-position.

The anomalous position of scillaridin-A has been partly removed by the demonstration[42] that this aglycone contains 24 carbon atoms in its molecule and not 25 as previously supposed, and that α-scillanic acid is identical with *allo*cholanic acid.[43]

Correlation of the toad poisons with the plant heart poisons has been established by the dehydrogenation of cinobufagin to 3′-methyl-1 : 2-*cyclo*pentenophenanthrene.[44] Molecular weight determinations of cinobufagin and two derivatives, employing *X*-ray crystallographic measurements, have shown[45] that this genin has the formula $C_{26}H_{34}O_6$, in close relationship to bufotalin $C_{26}H_{36}O_6$.[46] Chrysene has been obtained by selenium dehydrogenation of bufotalin,[46] and a provisional structure (LVI or LVII) has been assigned to bufotalin by H. Wieland, G. Hesse, and R. Hüttel,[47] who discuss its relationship to the other toad poisons. Essentially the same formulation has been proposed for cinobufagin by R. Tschesche and H. A. Offe,[48] who leave open the position of the acetoxy-group and the additional double bond.

Saponins.

These are glycosides of plant origin which have the property of forming colloidal aqueous solutions which foam on shaking. In addition, they are able to effect hæmolysis of the red blood cells, even in high dilution. Few of them are known in the pure state, but the sapogenins which result from their hydrolysis have been well characterised. These fall into two groups, of which one contains such triterpenes as hederagenin and oleanolic acid; these are dehydrogenated by selenium to mixtures of naphthalene and

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[42] A. Stoll, A. Hofmann, and J. Peyer, *Helv. Chim. Acta*, 1935, **18**, 1247.

[43] A. Stoll, A. Hofmann, and A. Helfenstein, *ibid.*, p. 644.

[44] H. Jensen, *J. Amer. Chem. Soc.*, 1935, **57**, 2733; R. Tschesche and H. Offe, *Ber.*, 1935, **68**, 1998.

[45] D. Crowfoot, *Chem. and Ind.*, 1935, **54**, 568; D. Crowfoot and H. Jensen, *J. Amer. Chem. Soc.*, 1936, **58**, 2018.

[46] H. Wieland and G. Hesse, *Annalen*, 1935, **517**, 22.

[47] *Ibid.*, 1936, **524**, 203.

[48] *Ber.*, 1936, **69**, 2361.

picene homologues, and do not come within the purview of this report. The other group contains sapogenins which are related in structure to the cardiac aglycones and sterols; some of the corresponding saponins occur with the cardiac glycosides in the leaves of *Digitalis purpurea.* The most important genins from digitalis are digitogenin, $C_{27}H_{44}O_5$, gitogenin, $C_{27}H_{44}O_4$, and tigogenin, $C_{27}H_{44}O_3$, derived from digitonin, gitonin, and tigonin, respectively.[49] Sarsasapogenin, $C_{27}H_{44}O_3$,[49] from sarsaparilla root, has also been extensively investigated. An isomeric compound, smilagenin, has recently been described.[50] It is surprising that these genins should be related to the characteristic animal sterol, cholesterol ($C_{27}H_{46}O$), rather than to the phytosterols, which contain 29 carbon atoms in their molecules.

W. A. Jacobs and J. C. E. Simpson showed that both sarsasapogenin [51] and gitogenin [52] give, on dehydrogenation with selenium, 3′-methyl-1 : 2-*cyclo*pentenophenanthrene and a ketone, $C_8H_{16}O$, not methyl *iso*hexyl ketone, which evidently represents a side chain common to these genins. The close structural relationship between the three digitalis genins was shown by R. Tschesche,[53] who found that chromic acid oxidation of both gitogenin and tigogenin leads, by opening of ring I, to gitogenic acid, which was also obtained by Wolff–Kishner reduction of the keto-dicarboxylic acid arising from the oxidation of digitogenin. Digitogenin, gitogenin, and tigogenin contain respectively three, two, and one secondary hydroxyl groups, the remaining two oxygen atoms being present in oxide rings.[54]

The relationship of the genins of the digitalis group to the sterols was completely demonstrated by R. Tschesche and A. Hagedorn,[55] who degraded the side chain of tigogenin (LVIII) and reduced the hydroxyl group in ring I (assumed to be at C_3) with the formation of ætio*allo*bilianic acid (LIX). F. A. Askew, S. N. Farmer, and G. A. R. Kon [50] conclude, on the basis of surface film measurements, that the hydroxyl group of sarsasapogenin is also at C_3, and not at C_{11} as originally suggested by J. C. E. Simpson and W. A. Jacobs,[56]

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[49] For revision of empirical formulæ, see J. C. E. Simpson and W. A. Jacobs, *J. Biol. Chem.*, 1935, **109**, 573; R. Tschesche and A. Hagedorn, *Ber.*, 1935, **68**, 1412.

[50] F. A. Askew, S. N. Farmer, and G. A. R. Kon, *J.*, 1936, 1399.

[51] *J. Biol. Chem.*, 1934, **105**, 501.

[52] *J. Amer. Chem. Soc.*, 1934, **56**, 1424.

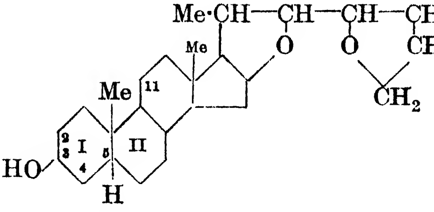
[53] *Ber.*, 1935, **68**, 1090; see also W. A. Jacobs and J. C. E. Simpson, *J. Biol. Chem.*, 1935, **110**, 429.

[54] Compare W. A. Jacobs and E. E. Fleck, *ibid.*, 1930, **88**, 545; A. Windaus, *Z. physiol. Chem.*, 1925, **150**, 205; *Nach. Ges. Wiss. Göttingen*, 1935, 89.

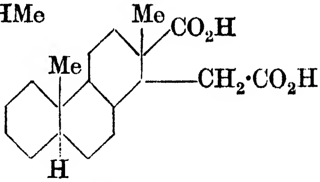
[55] *Ber.*, 1935, **68**, 1412.

[56] *J. Biol. Chem.*, 1935, **109**, 573.

a conclusion since supported by chemical evidence.[57] Using the method of Tschesche and Hagedorn, Kon and Farmer[58] have degraded sarsasapogenin to ætiobilianic acid, a result which proves that sarsasapogenin is a coprostane derivative, and indicates that it is stereoisomeric with tigogenin (LVIII), differing from it in the configuration with respect to C_5.



(LVIII.)



(LIX.)

The oxidation of gitogenin to gitogenic acid shows that the second hydroxyl group of this genin is at C_2 or C_4, and as the same acid is formed by oxidation of tigogenin (LVIII) belonging to the cholestane series, opening of the ring should occur between C_2 and C_3 (see p. 345). This and other evidence leads to the conclusion that the second hydroxyl group of gitogenin is at C_2. Both tigogenin[59] and sarsasapogenin[50] are precipitated by digitonin, so that the hydroxyl group at C_3 has the same configuration (*cis* to methyl at C_{10}) as in the sterols. Incidentally it is of interest that neither of the epimeric 4-cholesterols gives an insoluble compound with digitonin.[59]

The third hydroxyl group of digitogenin is placed at C_6. The earlier work on the degradation of this genin is reviewed by R. Tschesche and A. Hagedorn,[60] who interpret the reactions in terms of formula (LX). Thus the keto-dicarboxylic acid, digitogenic acid (LXI), resulting from the chromic acid oxidation of digitogenin[61] may be further oxidised by permanganate to a keto-tricarboxylic acid (LXII) in which ring II is opened. This is a β-keto-acid which readily eliminates a molecule of carbon dioxide, and by thermal decomposition loses a second molecule of carbon dioxide. These changes are expressed by the following partial formulæ, analogies for the later stages being given by the experiments of H. Lettré,[62]

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[57] Private communication from Dr. Kon.

[58] *Chem. and Ind.*, 1936, **55**, 925.

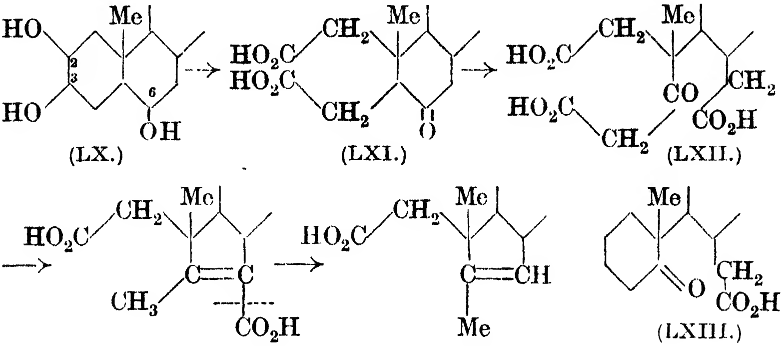
[59] R. Tschesche and A. Hagedorn, *Ber.*, 1935, **68**, 2247.

[60] *Ber.*, 1936, **69**, 797.

[61] See, for example, H. Kiliani, *Ber.*, 1916, **49**, 701; 1918, **51**, 1613; A. Windaus and K. Weil, *Z. physiol. Chem.*, 1922, **121**, 62; A. Windaus and U. Willerding, *ibid.*, 1925, **143**, 33.

[62] *Ibid.*, 1933, **218**, 67; **221**, 73.

who, for example, obtained an unsaturated hydrocarbon by pyrolysis of a keto-acid of type (LXIII) formed by oxidation of Δ^5-cholestene :



The evidence for the structure of the side chain present in this group of sapogenins (see formula LVIII) has been summarised by L. F. Fieser[1] (p. 341), in which connexion reference should also be made to the critical discussion by Tschesche and Hagedorn.[60]

By no means the least interesting development in the chemistry of the sterol group is the recognition that there is a class of alkaloids containing the sterol ring system, the side chain at C_{17} being utilised in the formation of heterocyclic systems containing nitrogen. Reference to these compounds is made in another section of this Report.

J. W. C.

8. HETEROCYCLIC COMPOUNDS.

Large Oxygen Rings.—Large rings containing oxygen have been prepared for the first time by M. Stoll and W. Scherrer.[1] The mono-sodium derivative of tetradecane-1 : 14-diol was treated with one equivalent of benzenesulphonyl chloride, and the resulting ester (I) was treated with sodium in boiling benzene (the sodium, to be effective in this reaction, must be very finely divided, and the authors prepared it by passing strictly dry ammonia into a mixture of sodium and toluene, cooled in ether and solid carbon dioxide. When the metal had dissolved, the ammonia was allowed to evaporate; the sodium slowly formed very reactive, minute crystals). Under these conditions, the benzenesulphonyl derivative passes into its sodium derivative (II), which partly cyclises to 1 : 14-oxidotetradecane (oxa*cyclo*pentadecane) (III). Since (II) can only be formed slowly,

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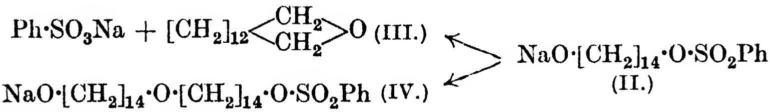
[1] *Helv. Chim. Acta*, 1936, **19**, 735.

(I) has plenty of time to undergo side reactions, *e.g.*, to give (IV). As a result, the yield of (III) is poor.

$$OH\cdot[CH_2]_{14}\cdot ONa + Ph\cdot SO_2Cl \longrightarrow OH\cdot[CH_2]_{14}\cdot O\cdot SO_2Ph \quad \text{(I.)}$$



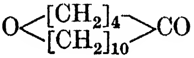
$$Ph\cdot SO_3Na + [CH_2]_{12}{<}\substack{CH_2\\CH_2}{>}O \ \text{(III.)} \longleftarrow NaO\cdot[CH_2]_{14}\cdot O\cdot SO_2Ph \ \text{(II.)} \longrightarrow NaO\cdot[CH_2]_{14}\cdot O\cdot[CH_2]_{14}\cdot O\cdot SO_2Ph \ \text{(IV.)}$$

$$2OH\cdot[CH_2]_{14}\cdot O\cdot SO_2Ph \rightleftharpoons OH\cdot[CH_2]_{14}\cdot OH + Ph\cdot SO_2\cdot O\cdot[CH_2]_{14}\cdot O\cdot SO_2Ph \longrightarrow \text{(IV)}$$

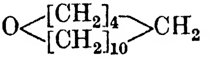
A second method was to begin as follows :

$$OH\cdot[CH_2]_3\cdot O\cdot[CH_2]_{10}\cdot CO_2Me \longrightarrow Cl[CH_2]_3\cdot O\cdot[CH_2]_{10}\cdot CO_2Me \longrightarrow (CO_2Et)_2CH\cdot[CH_2]_3\cdot O\cdot[CH_2]_{10}\cdot CO_2Me \longrightarrow CO_2H\cdot[CH_2]_4\cdot O\cdot[CH_2]_{10}\cdot CO_2H \quad \text{(V.)}$$

Distillation of the cerium salt of the acid (V) gave 1 : 15-oxidopentadecan-5-one (VI), and this was reduced by the Wolff-Kishner process

(VI.) 

$$O{<}\substack{[CH_2]_4\\[CH_2]_{10}}{>}CO$$

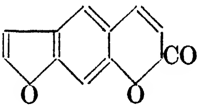
 (VII.)

$$O{<}\substack{[CH_2]_4\\[CH_2]_{10}}{>}CH_2$$

to 1 : 15-oxidopentadecane (oxa*cyclo*hexadecane) (VII). The two oxa*cyclo*compounds are low-melting solids, with a very feeble musk-like odour ; the oxide-ketone (VI), which is isomeric with "exaltolide" (ξ-hydroxypentadecoic acid lactone),[2] has a powerful odour of musk, although of a modified type.

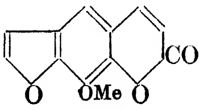
G. Salomon[3] has considered the kinetics of the formation of large rings of the cyclic imine and lactone series.

Naturally Occurring Oxygen Ring Compounds.—Psoralene, from the oil of *Psoralea corylifolia* seeds, is (VIII), since the usual degradative methods (methylation ; oxidation ; methylation)[4] lead to methyl 4 : 6-dimethoxy*iso*phthalate (IX). A substance, ficusin, apparently identical with psoralene, has been extracted by K. Okahara[5] from the leaves of *Ficus carica.*



(VIII.)

(IX.)



(X.)

Xanthotoxin, isolated from *Fagara xanthoxyloides* and various *Rutaceae,* is the methoxy-derivative (X) of psoralene (ficusin).[6]

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[2] L. Ruzicka and M. Stoll, *Helv. Chim. Acta,* 1928, **11**, 1159.

[3] *Ibid.*, 1936, **19**, 743.

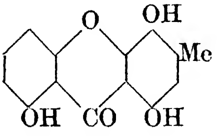
[4] E. Späth, B. L. Manjunath, M. Pailer, and H. S. Jois, *Ber.*, 1936, **69**, 1087.

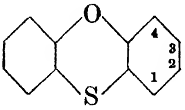
[5] *Bull. Chem. Soc. Japan,* 1936, **11**, 389.

[6] E. Späth and M. Pailer, *Ber.*, 1936, **69**, 767.

H. Raistrick, R. Robinson, and D. E. White [7] have investigated a yellow pigment, ravenelin, produced during the metabolism of the plant *Helminthosporium Ravenelii*, Curtis, and of *H. Turcicum*, Passerini. The pigment is shown to be 1 : 4 : 8-trihydroxy-3-methylxanthone (XI), and is the third hydroxyxanthone to be isolated from natural sources, euxanthone and gentisin being the other two representatives of this class.

(XI.)





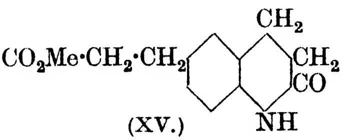
(XII.)

Phenoxthionin.—It has been shown [8] that bromination, sulphonation, and condensation with acyl chlorides (Friedel–Crafts) occurs in the 2-position in phenoxthionin (XII), the orienting effect of the oxygen thus outweighing that of the sulphur.

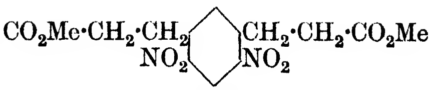
Reduced Dipyridinobenzenes.—Some interesting results have been obtained by P. Ruggli and A. Staub.[9] When *m*-phenylenediacrylic acid is nitrated, 4-nitration occurs (contrast cinnamic acid). Reduction of the nitro-compound (XIII) is unaccompanied by cyclisation, suggesting that the amino-acid (XIV) has the *trans*-configuration. Methyl *m*-phenylenediacrylate also gives only one nitro-derivative (as XIII), which, catalytically reduced, (*a*) in the cold, gives the methyl ester of (XIV), and (*b*) in the warm, gives methyl 2-ketotetrahydroquinoline-6-propionate (XV), ring closure occurring spontaneously.

(XIII.)

(XIV.)



(XV.)



(XVI.)

In order to introduce a second nitro-group at the outset, it was found necessary to reduce the *m*-diacrylic ester to the *m*-dipropionic ester. The latter was readily dinitrated to give (XVI). Reduction of this ester, curiously enough, produced (XVII), and in order to effect

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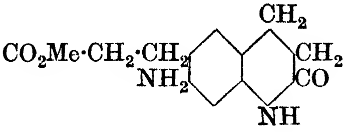
[7] *Biochem. J.*, 1936, **30**, 1303.

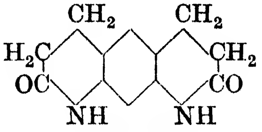
[8] C. M. Suter, J. P. McKenzie, and C. E. Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 717.

[9] *Helv. Chim. Acta*, 1936, **19**, 439.

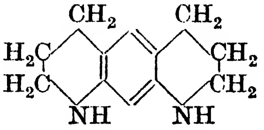
ring closure in the 6 : 7-positions it was necessary to heat (XVII) to 260°, or to treat it with boiling hydrochloric acid for some time. The product (XVIII) was unaffected by distillation with zinc dust, and the well-known method of reduction, starting with NH·CO ⟶ N:CCl, could not be applied. Recourse was made to the classical reduction with phosphorus and hydriodic acid under pressure, but even this reaction only gave good results within a very narrow temperature range. The reduced dipyridinobenzene (XIX) obtained is a crystalline solid.



(XVII.)



(XVIII.)



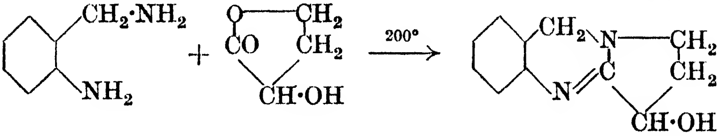
(XIX.)

E. E. T.

9. Alkaloids.

Peganine (*Vasicine*).—The optical resolution of peganine was effected by E. Späth, F. Kuffner, and N. Platzer,[1] who thought the alkaloid probably existed in the active condition in *Peganum harmala*, but did not succeed in isolating it as such. A. D. Rosenfeld and D. G. Kolesnikov [2] found that the active alkaloid can be extracted from the plant, and in their later paper regard their product as probably identical with the *l*-peganine isolated by E. Späth and F. Kesztler [3] from *Adhatoda vasica*, Nees.

A simple synthesis of peganine (I) has been described : [4]



(I.)

The interesting work of Schöpf and his co-workers on syntheses "under physiological conditions" has been extended to vasicine.[5] It is found that *o*-aminobenzaldehyde, allylamine, and formaldehyde,

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[1] *Ber.*, 1935, **68**, 1384.

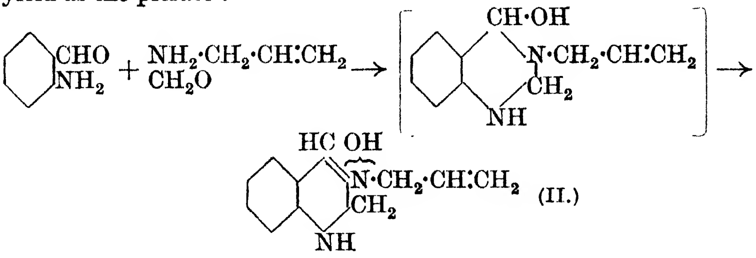
[2] *Sixth Mendeléeff Congress*, 1932; *Ber.*, 1936, **69**, 2022.

[3] *Ber.*, 1936, **69**, 384.

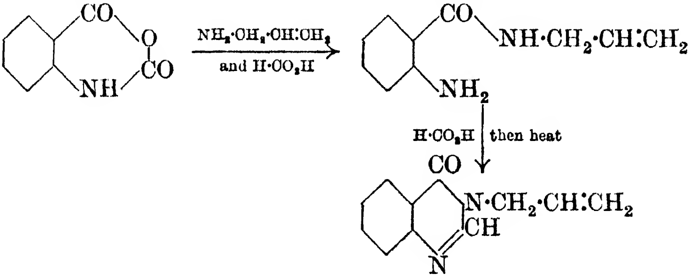
[4] E. Späth and N. Platzer, *ibid.*, p. 255.

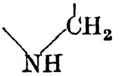
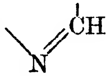
[5] C. Schöpf and F. Oechler, *Annalen*, 1936, **523**, 1.

when left together in aqueous solution for three days at 25°, condense as in the annexed scheme, the product (II) being isolated in 73% yield as the picrate :

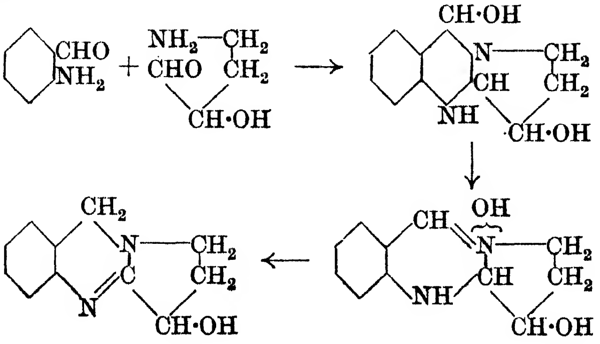

(II.)

The synthesis begins at p_H 4·8 and ends at p_H 5·2, and proceeds similarly in phosphate-buffered solution at p_H 7. The constitution of (II) is proved by the oxidation of its picrate to the picrate of 3-allyl-4-quinazolone, prepared independently from isatoic anhydride :

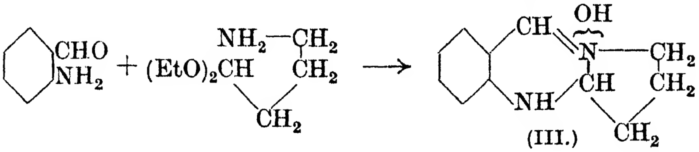


Moreover, the oxidation of  to  can be effected under physiological conditions, by using potassium ferricyanide and a phosphate buffer at p_H 7 at the ordinary temperature.

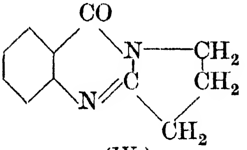
It is concluded that the actual bio-synthesis of vasicine probably occurs between *o*-aminobenzaldehyde and γ-amino-α-hydroxybutaldehyde :

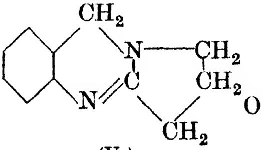


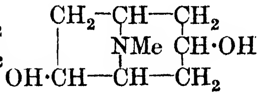
Since the aminohydroxybutaldehyde is unknown, the authors carried out the analogous synthesis (citrate buffer, 4 days, p_H 5):


(III.)

and obtained (III) in 75—78% yield, as the picrate. Its constitution was established by its oxidation to the known compound [6] (IV). Further, if a condensation mixture containing (III) was shaken with palladium and hydrogen, the originally yellow solution was decolorised and deoxyvasicine (V) could be isolated in 18% yield, suggesting that biogenetic synthesis probably proceeds along these lines. The authors think it likely that the precursor in the plant of the *o*-aminobenzaldehyde is tryptophan, and that of the γ-amino-α-hydroxybutaldehyde is hydroxyornithine:


(IV.)


(V.)


(VI.)

$$\begin{tikzcd}
 & CO_2H{\cdot}CH(NH_2){\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \arrow[dl] \arrow[dr] & \\
CHO{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 & & CHO{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H
\end{tikzcd}$$

C. Schöpf and G. Lehmann [7] had already suggested that the hydroxytropine (VI) isolated by O. Wolfes and H. Hromatka [8] from coca leaves owed its biogenetic synthesis to malic dialdehyde, and this, and the aminohydroxybutaldehyde, would both come from hydroxyornithine. This may be compared with the derivation of hygrine and cuskhygrine from ornithine.

Lupin Alkaloids.—in 1931, G. R. Clemo and G. R. Ramage [9] synthesised octahydropyridocoline (VIII) by performing a Dieckmann condensation on (VII). The product was not identical with norlupinane (A) obtained from lupinine.[10] Later,[11] however,

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[6] R. C. Morris, W. E. Hanford, and R. Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 951.

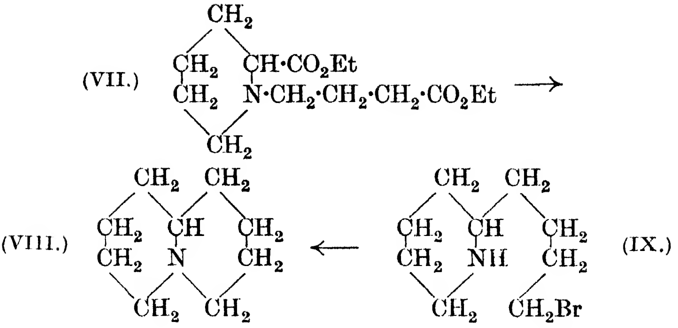
[7] *Annalen*, 1935, **518**, 1.

[8] *Mercks Jahresber.*, 1934, **47**, 45.

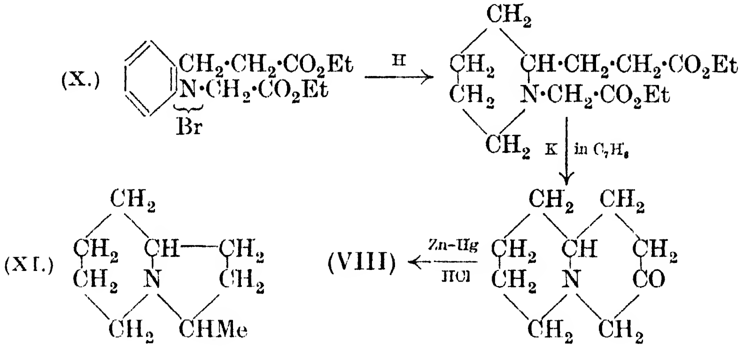
[9] *J.*, 437; *Ann. Reports*, 1931, 174.

[10] G. R. Clemo, G. R. Ramage, and R. Raper, *J.*, 1931, 437, 3190.

[11] *Idem*, *J.*, 1932, 2959.



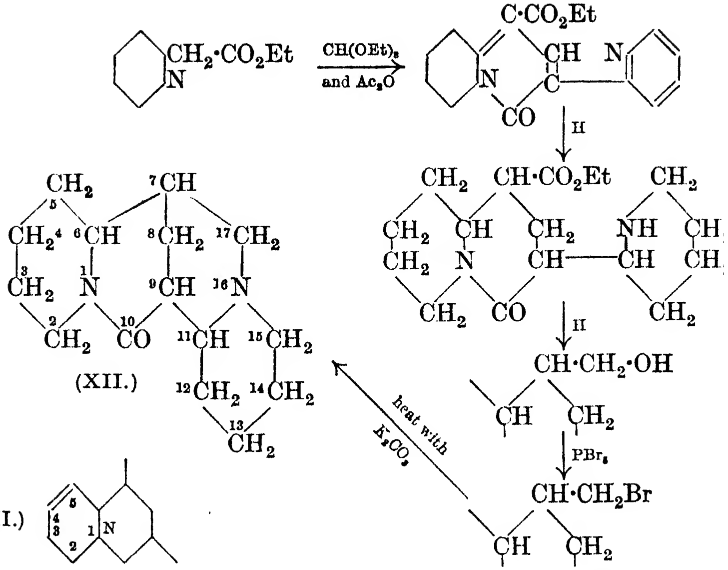
norlupinane (A) was obtained by cyclisation of (IX) and more recently [12] as follows :



This dismisses the possibility that norlupinane (A) is (XI), and substantiates the *cis-trans* relationship of the two octahydropyridocolines (VIII) obtained from (VII) and from (IX) or (X). It has been established by synthesis [13] that *dl*-oxysparteine is (XII).

K. Winterfeld and H. E. Rönsberg,[14] by oxidising α-didehydrosparteine with chromic anhydride, have isolated β-aminopropionic acid, which is regarded as indicating the presence (see XIII) of a 4 : 5-ethylenic linkage in the norlupinane ring of sparteine. When didehydrosparteine is treated with benzoyl chloride and alkali, an unstable benzoyl derivative is formed, suggesting that the second ethylenic linkage is in the αβ-position to a nitrogen atom, and is joined to a tertiary carbon atom. This corresponds with unsaturation at C_9—C_{11} or C_{11}—C_{12}.

[12] G. R. Clemo, W. McG. Morgan, and R. Raper, *J.*, 1935, 1743.
[13] *Idem, J.*, 1936, 1025.
[14] *Arch. Pharm.*, 1936, **274**, 48.



(XII.)

(XIII.)

Ergot Alkaloids (continued from *Ann. Reports*, 1935, 345).—In an examination of their proposed constitution of lysergic acid, W. A. Jacobs and L. C. Craig [15] synthesised 3 : 4 : 5 : 6-tetrahydro-4-carboline-5-carboxylic acid and 3-phenyl-4-methyltetrahydro-4-carboline-5-carboxylic acid. These substances did not respond to tests characteristic of lysergic acid. Later,[16] a new formula was suggested for this substance, since the tribasic acid, $C_{14}H_9O_8N$, previously described [17] gave quinoline when it was distilled with soda-lime. The same authors [18] have confirmed their previous conclusion [19] that ergotamine, and therefore ergotaminine, are derived from ergine, proline, phenylalanine and pyruvic acid. They have also isolated *d*-proline (as its methyl ester) by hydrolysis not only of ergotamine but also of ergotoxine. Ergoclavine is given the new formula $C_{25}H_{30}O_4N_4$. It is possible that this alkaloid is built up from ergine, *l*-leucine and pyruvic acid, but very little is really known.

S. Smith and G. M. Timmis [20] have shown that ergometrinine, like ergometrine, is lysergic acid hydroxy*iso*propylamide. The same authors [21] have obtained from ergot a new alkaloid, ergosinine,

[15] *Science*, 1935, **82**, 421.
[16] *Ibid.*, 1936, **83**, 38.
[17] *J. Biol. Chem.*, 1932, **97**, 739.
[18] *J. Org. Chem.*, 1936, **1**, 245.
[19] *Science*, 1935, **81**, 256.
[20] *J.*, 1936, 1166.
[21] *Nature*, 1936, **137**, 111, 1075.

$C_{30}H_{35}O_5N_5$, which is converted by acids into the isomeric ergosine.

R. L. Grant and S. Smith [22] have found that ergometrine exists in two physical forms.

G. W. Holden and G. R. Diver [23] have isolated from ergot yet another alkaloid, ergomonamine, $C_{19}H_{19}O_4N$, and an acid (citergic), which may be ααβγ-tetrahydroxypropane-αβγ-tricarboxylic acid.

It is now agreed [24] that ergometrine, ergotocine, ergobasine and ergostetrine are identical.

S. Smith and G. M. Timmis [25] have used conditions (hot alcoholic phosphoric acid) under which ergotinine changes into ergotoxine for the conversion of ergine ($[\alpha]_{5461}$ + 635°, in pyridine) into the new isomeric base, *iso*ergine ($[\alpha]_{5461}$ + 25°), and conclude that the physiologically active (lævorotatory) alkaloids ergotoxine, ergotamine, and ergometrine contain the *iso*ergine structure. They further showed that alkalis rapidly isomerise ergine and *iso*ergine to an equilibrium mixture. Again, using the conditions (action of pyridine, or hot methyl alcohol, or hot ethyl alcohol, or sodium hydroxide) effecting the change of ergotoxine into ergotinine, or, better, by the action of hot water, the authors have succeeded in converting lysergic acid into an isomeride, *iso*lysergic acid. The latter has $[\alpha]_{5461}$ + 365°, as compared with $[\alpha]_{5461}$ + 49° for lysergic acid. Possible partial formulæ are suggested for lysergic acid, based on one put forward, but since rejected, by W. A. Jacobs and L. C. Craig.[26]

W. A. Jacobs and L. C. Craig [27] also point out that the existence of the pairs of ergot alkaloids depends on the ethylenic linkage in lysergic acid, since, while methyl lysergate mutarotates in warm methyl-alcoholic solution, its dihydro-derivative does not. A fresh method of attacking the problem is described by these authors, who have obtained one and the same lysergic acid by hydrolysing any of the alkaloids, whether of the dextro- or of the lævo-rotatory class. On the other hand, reduction (2H) of the lævorotatory alkaloids ergotoxine, ergotamine, and ergometrine, followed by hydrolysis, gave a lævorotatory acid, called α-dihydrolysergic acid; similar treatment of the dextrorotatory alkaloids ergotinine and ergotaminine and also of ergine gave a dextrorotatory acid, γ-dihydrolysergic acid. Lysergic acid is not a mixture, but when it is reduced,

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[22] *Nature*, 1936, **137**, 154.

[23] *Quart. J. Pharm.*, 1936, **9**, 230.

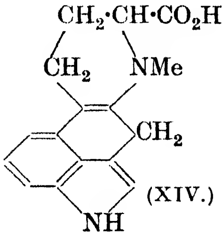
[24] M. S. Kharasch, H. King, A. Stoll, and M. R. Thompson, *Nature*, 1936, **137**, 403; *Science*, 1936, **83**, 206; *Ann. Reports*, 1935, 349.

[25] *J.*, 1936, 1440.

[26] *J. Biol. Chem.*, 1936, **113**, 771.

[27] *Ibid.*, **115**, 227.

it gives a mixture of the above α- and γ-dihydro-derivatives. The authors conclude that in this reduction new centres of asymmetry are produced, and suggest that lysergic acid is (XIV), since this best accounts for the production of two dihydro-derivatives, and for the stability of lysergic acid in presence of alkali. The above α-dihydro-acid (from ergotoxine) was identical with that previously obtained by reducing lysergic acid with sodium and amyl alcohol; its methyl ester, on reduction with sodium and butyl alcohol, gave α-dihydrolysergol; but methyl γ-dihydrolysergate, similarly reduced, gave a new substance, γ-dihydrolysergol, different from the β-dihydrolysergol obtained previously from ergotinine. Neither methyl α- nor γ-dihydrolysergates gave β-dihydrolysergol on reduction.



(XIV.)

Aconitine.—Some advance has been made in the chemistry of this difficult alkaloid. A. Lawson [28] has oxidised aconitine with chromic anhydride in acetone solution, and obtained a new substance, aconitoline, $C_{17}H_{16}O(NMe)(OH)(OMe)_3(OAc)(OBz)$. The author's results support the formula $C_{32}H_{43}O_{12}N$ of E. Späth and F. Galinovsky [29] for oxonitin. W. Freudenberg and E. F. Rogers [30] showed that dry distillation of aconitine hydrochloride with barium hydroxide gave hydrocarbons, methylamine, and *l*-ephedrine, the structure of the last therefore probably being present in aconitine. It has usually been *assumed* that aconitine contains the NMe group, but it is now found [31] that when aconitine hydrochloride is fused with potassium or barium hydroxide, ethylamine is formed, and when aconitine is heated with hydriodic acid ethyl as well as methyl iodide is obtained. It is thought that the NEt group is affected when aconitine is oxidised to oxonitin. This would fit in with the observed formation of acetaldehyde during this oxidation. W. Freudenberg [32] has also identified ethylamine among the products of distilling aconitine with barium hydroxide, and gives the alkaloid the formula $C_{19}H_{19}(NEt)(OH)_3(OMe)_4(OAc)(OBz)$.

Veratrum Alkaloids.—B. K. Blount [33] showed that the verine of C. R. A. Wright and A. P. Luff [34] was identical with cevine (veratridine being veratroylcevine), and that cevine, when dehydrogenated

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[28] *J.*, 1936, 80.

[29] *Ber.*, 1930, **63**, 2994; 1931, **64**, 2201.

[30] *J. Amer. Chem. Soc.*, 1936, **58**, 533.

[31] W. A. Jacobs and R. C. Elderfield, *ibid.*, p. 1059.

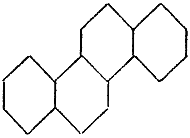
[32] *Ber.*, 1936, **69**, 1962.

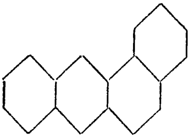
[33] *J.*, 1935, 122.

[34] *J.*, 1878, **33**, 341.

with selenium, gave a base, cevanthridine, possibly a phenanthridine derivative. In conjunction with (Miss) D. Crowfoot[35] the same author isolated cevanthrol, a phenol, from the dehydrogenation mixture, and concludes further, from *X*-ray crystallographical examination, that cevanthridine contains a benzphenanthrene (XV) or benzanthracene (XVI) structure. The authors regard the conditions employed in the dehydrogenation as insufficiently drastic to be conducive to ring enlargement, that is, they appear to have considered, but rejected, the idea that cevanthridine might contain a methyl*cyclo*pentenophenanthrene skeleton.

(XV.)





(XVI.)

Veratrum album (white hellebore) contains the alkaloid jervine, $NH{:}C_{25}H_{33}(OH)(CH_2O_2{:})$, and amorphous materials of various kinds from which both angelic and tiglic acids have been isolated.[36]

Heliotropium *and* Senecio *Alkaloids*.—G. Menschikov[37] isolated from *Heliotropium lasiocarpum* an alkaloid heliotrine, $C_{16}H_{27}O_5N$, which by the action of barium hydroxide gave heliotric acid, $OH{\cdot}C_6H_{11}(OMe)(CO_2H)$ (a saturated aliphatic acid), and heliotridine, $C_8H_{13}O_2N$. The latter[38] contains two hydroxyl groups, replaceable (thionyl chloride) by two chlorine atoms. The (unstable) dichloro-compound was converted by a series of simple reactions into heliotridan, $C_8H_{15}N$. Later work showed that heliotrine was reducible to hydroxyheliotridan, which was probably a tertiary alcohol,[39] and that heliotridan contained a pyrrolidine ring.[40] The same author, with V. Rubinstein,[41] has also isolated from *Trichodesma incanum* the alkaloid trichodesmine, $C_{18}H_{27}O_6N$. This with alkali gave methyl *iso*butyl ketone, *dl*-lactic acid, and a substance, $C_8H_{13}O_2N$, trichodesmidine, which was not identical with heliotridine, but was convertible by simple reactions into heliotridan. Heliotridine and trichodesmidine therefore differ in the position of the hydroxyl group and possibly also that of the ethylenic linkage. Later[42] it was found that lasiocarpine, a second alkaloid

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[35] *J.*, 1936, 414.

[36] K. Saito, H. Suginome, and M. Takaoka, *Bull. Chem. Soc. Japan*, 1934, **9**, 15; K. Saito and H. Suginome, *ibid.*, 1936, **11**, 168; K. Saito and M. Takaoka, *ibid.*, p. 172.

[37] *Ber.*, 1932, **65**, 974.

[38] G. Menschikov, *Ber.*, 1933, **66**, 875.

[39] *Ber.*, 1935, **68**, 1051.

[40] *Ibid.*, p. 1555.

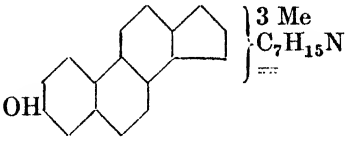
[41] *Ibid.*, p. 2039.

[42] G. Menschikov and J. Schdanowitsch, *Ber.*, 1936, **69**, 1110.

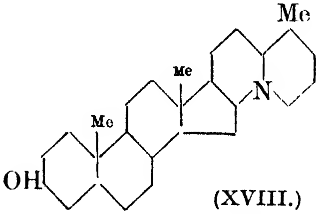
from *Heliotropium lasiocarpum*, was hydrolysed by alkali to angelic acid and heliotridine. In heliotrine, only one hydroxyl group of heliotridine is esterified (with heliotric acid), whereas in lasiocarpine one hydroxyl group of heliotridine is esterified with angelic acid and the other with lasiocarpic acid, $C_8H_{16}O_5$: this is an unsaturated acid containing two hydroxyl and two methoxyl groups.

Senecio platyphyllus contains two alkaloids, platyphylline, $C_{18}H_{27}O_5N$, and seneciphylline.[43] Platyphylline on alkaline hydrolysis gave platynecic acid, $OH{\cdot}C_9H_{12}O{\cdot}CO_2H$, and platynecine, $C_8H_{13}N(OH)_2$. The two hydroxyl groups can under certain conditions be replaced by chlorine, and by simple reactions the authors converted the dichloro-compound into heliotridan. Apparently seneciphylline is also derived from this substance. The *Boraginaceæ* (*Heliotropium*) and *Senecio* alkaloids therefore contain the same $C_8H_{15}N$ skeleton and differ in their degree of unsaturation, the position of the hydroxyl groups, and the nature of the attached acids.

Solanum *Alkaloids*.—Solanidine-*t* (from the potato, *Solanum tuberosum*), when heated with selenium, gives phenanthrene, chrysene, and pyridine, together with other compounds.[44] A. Soltys and K. Wallenfels [45] have shown that solaneine, described as occurring with solanine, solanidine, and solanthrene in *S. tuberosum*, is a mixture of solanidine and solanine. Having found that solanidine gives a flocculent precipitate with digitonin in alcoholic solution, a reaction characteristic of sterols, they further found that selenium dehydrogenation of solanidiene (obtained by elimination of water from solanidine) gave methyl*cyclo*pentenophenanthrene. From this, it follows that solanidine-*t* is (XVII), and the authors think that a possible formula for the alkaloid is (XVIII).



(XVII.)



(XVIII.)

Solanidine-*s*, from *S. sodomæum*, contains structure (XIX),[46] a fact which explains the formation of " tetra-acetylsolanidine " when

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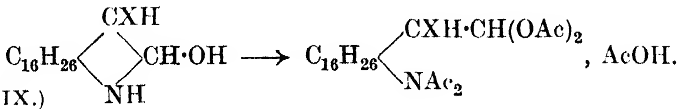
[43] A. Orékhov, *Ber.*, 1935, **68**, 650; A. Orékhov and R. Konovalowa, *ibid.*, p. 1186; R. Konovalowa and A. Orékhov, *Ber.*, 1936, **69**, 1908.

[44] H. Dieterle and H. Rochelmeyer, *Arch. Pharm.*, 1935, **273**, 532.

[45] *Ber.*, 1936, **69**, 811.

[46] G. Oddo and G. Caronna, *ibid.*, p. 283.

the alkaloid is treated with a mixture of glacial acetic acid, acetic anhydride, and concentrated sulphuric acid :



$$\mathrm{C_{16}H_{26}}\left\langle\begin{matrix}\mathrm{CXH}\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{CH{\cdot}OH} \longrightarrow \mathrm{C_{16}H_{26}}\left\langle\begin{matrix}\mathrm{CXH{\cdot}CH(OAc)_2}\\ \mathrm{NAc_2}\end{matrix}\right., \mathrm{AcOH}.$$

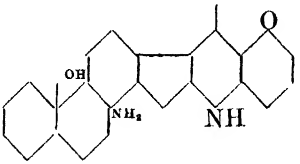
(XIX.)

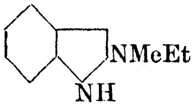
Solanum pseudocapsicum (winter cherry) may, like other *Solanums*, contain a gluco-alkaloid, but this is not settled. The new alkaloids, solanocapsine, $C_{25}H_{42}O_2N_2$ or $C_{26}H_{44}O_2N_2$, and solanocapsidine, probably $C_{26}H_{42}O_4N_2$, have been isolated from it, and the former has been investigated.[47] Solanocapsine contains NH, NH_2, and OH (probably as ⁝C·OH), the second oxygen probably being a member of a heterocyclic ring. With nitrous acid, the NH is nitrosated, the amino-group becomes hydroxyl, one hydroxyl group, probably the one originally present, is eliminated as water, and an ethylenic linkage is formed. Selenium dehydrogenation of solanocapsine gives hydrocarbons, pyridine bases, and methyl*cyclo*pentenophenanthrene. This suggests that the structure of the alkaloid is approximately expressed by formula (XX).

The position of the ring oxygen atom recalls the oxygen bridge in certain saponins of *Digitalis*.[48] Solangustidine, $C_{27}H_{43}O_2N$,[49] differs from solanidine-*t* in having an extra oxygen atom, and in solanocapsine this difference is increased by an additional nitrogen atom (amino-group).

I. Z. Saiyed and D. D. Kanga [50] have isolated from *Solanum xanthocarpum* a sterol, $C_{36}H_{54}O$ (carpesterol), an alkaloid, solancarpidine, $C_{26}H_{43}O_3N$, and a gluco-alkaloid, solancarpine, $C_{44}H_{77}O_{19}N$, which, on hydrolysis, gives solancarpidine, glucose, rhamnose, and (probably) galactose.

(XX.)





(XXI.)

Indole Derivatives.—A base, gramine, was isolated from a chlorophyll-defective strain of barley by H. von Euler and H. Hellström.[51]

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[47] G. Barger and H. L. Fraenkel-Conrat, *J.*, **1936**, 1537.

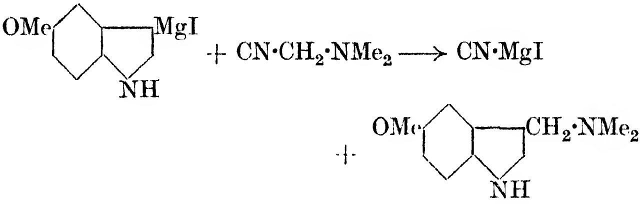
[48] Cf. J. C. E. Simpson and W. A. Jacobs, *J. Biol. Chem.*, 1935, **109**, 573; R. Tschesche and A. Hagedorn, *Ber.*, 1935, **68**, 1412; 1936, **69**, 797.

[49] F. Tutin and H. W. B. Clewer, *J.*, 1914, **105**, 559.

[50] *Proc. Indian Acad. Sci.*, 1936, **4**, 283.

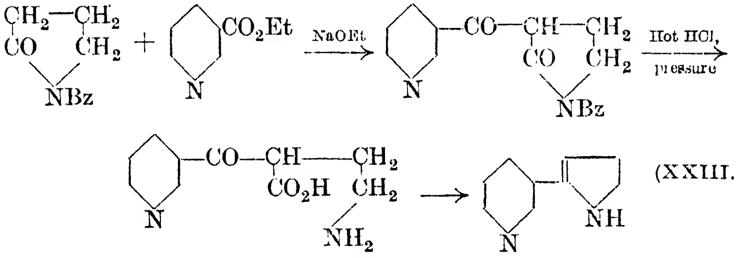
[51] *Z. physiol. Chem.*, **1933**, **217**, 23.

It was later thought to be identical with donaxine, isolated [52] from *Arundo donax*, and regarded as (XXI), but no proof of constitution was put forward. T. Wieland and C. Y. Hsing [53] have synthesised 5-methoxy-3-dimethylaminomethylindole (XXII), which appears to be identical with gramine, although the methiodide has a much higher melting point than that of the natural substance :



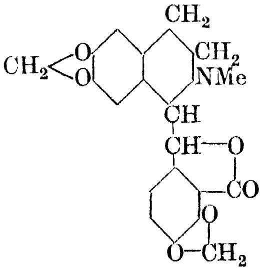
(XXII.)

Tobacco Alkaloid.—Myosmine (XXIII), one of the tobacco alkaloids, has been synthesised [54] as follows :

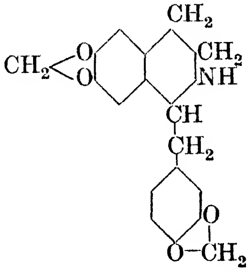


(XXIII.)

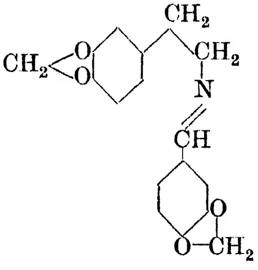
*iso**Quinoline Alkaloids.*—A synthesis has been recorded [55] of *dl*-bicuculline (XXIV), the *d*-form of which was isolated by R. H. F. Manske [56] from *Dicentra cucullaria*, *Adlumia fungosa*, *Corydalis sempervirens*, and *C. aurea.*



(XXIV.)



(XXV.)



(XXVI.)

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[52] A. Orékhov and S. Norkina, *Ber.*, 1935, **68**, 436.

[53] *Annalen*, 1936, **526**, 188.

[54] E. Späth and L. Mamoli, *Ber.*, 1936, **69**, 757.

[55] P. W. G. Groenewoud and R. Robinson, *J.*, 1936, 199.

[56] *Canadian J. Res.*, 1932, **7**, 258, 265; 1933, **8**, 142.

It has been stated [57] that the compound obtained " under physiological conditions " by G. Hahn and O. Schales [58] is not (XXV) but (XXVI). The last-named authors [59] have, however, replied satisfactorily to the criticism.

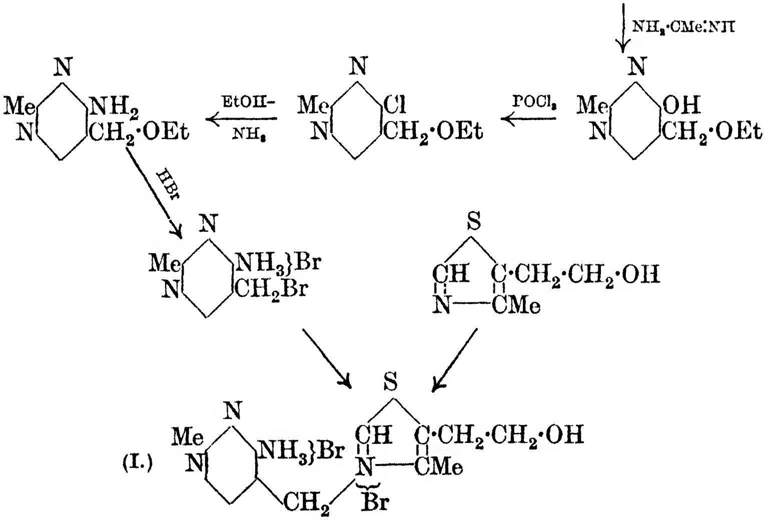
Tropinone Derivative.—Although there are many recorded cases in which Claisen condensations between carbonic esters and ketones or ketonic esters have given very indifferent yields, it has now been found [60] that tropinone reacts vigorously with methyl or ethyl carbonate in presence of sodium or potassium, preferably when benzene or xylene is used as a medium. It thus becomes possible to prepare tropinonecarboxylic esters quickly and in good yields.

E. E. T.

10. VITAMIN B_1 (ANEURIN) AND THIOCHROME.

Vitamin B_1 (I) has been synthesised by R. R. Williams and J. K. Cline[1], according to the scheme :

$$CO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}OEt \xrightarrow{H{\cdot}CO_2Et} CO_2Et{\cdot}CH(CHO){\cdot}CH_2{\cdot}OEt$$



The chloride was identical with the natural substance in ultra-violet absorption and antineuritic potency, but had a melting point of 232—234°, whereas the natural product melts at 246°. Possibly the latter is a mixture of stereoisomerides.

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[57] E. Späth, F. Kuffner, and F. Kesztler, *Ber.*, 1936, **69**, 378.

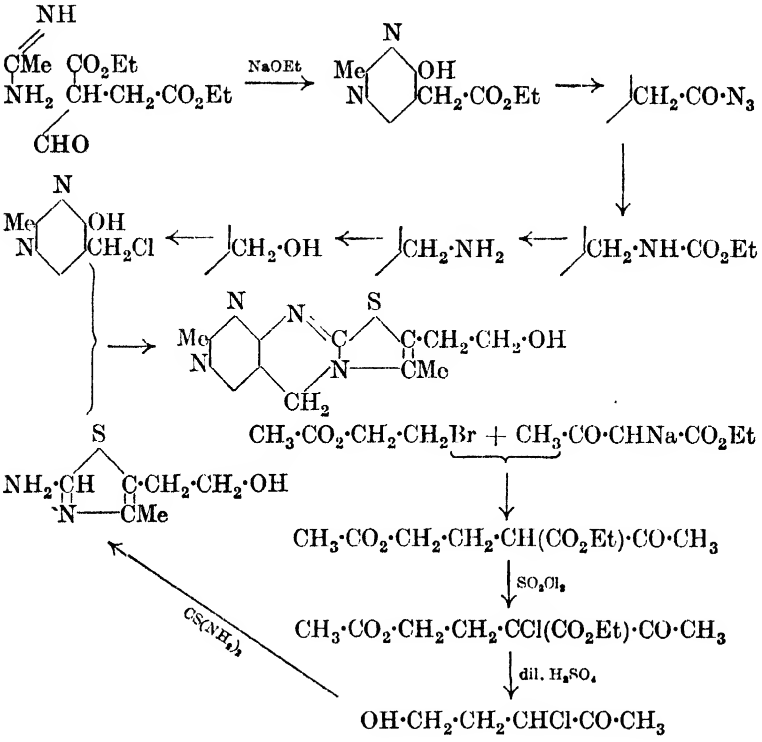
[58] *Ber.*, 1935, **68**, 24.

[59] *Ber.*, 1936, **69**, 622.

[60] N. A. Preobrashenski, M. N. Schtschukina, and R. A. Lapina, *ibid.*, p. 1615.

[1] *J. Amer. Chem. Soc.*, 1936, **58**, 1504.

A. R. Todd and F. Bergel[2] proposed formula (II) for thiochrome (obtained by the action of alkaline ferricyanide[3] or of alkali alone[4] on aneurin) and later, with H. L. Fraenkel-Conrat and Miss A. Jacob,[5] effected its synthesis :



The end-product of the synthesis was in all respects identical with thiochrome as obtained from vitamin B_1.

E. E. T.

W. BAKER.
J. W. COOK.
R. D. HAWORTH.
E. L. HIRST.
R. P. LINSTEAD.
S. PEAT.
E. E. TURNER.

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[2] *J.*, 1936, 1559.

[3] G. Barger, F. Bergel, and A. R. Todd, *Ber.*, 1935, **68**, 2257.

[4] R. Kuhn and H. Vetter, *ibid.*, p. 2375.

[5] *J.*, 1936, 1601.

BIOCHEMISTRY.

This year has seen further definite progress in the isolation of substances belonging to the groups of hormones and vitamins. The constitution of vitamin B_1 has been established beyond doubt; for the first time a substance with anti-rachitic properties has been isolated from natural sources; a cyclic alcohol, apparently pure, with the activity associated with vitamin E has been isolated; and of a number of sterol-like substances obtained from the adrenals, one is highly active in the manner characteristic of the cortical hormone. The anti-anæmic factor in liver has not yet, apparently, been obtained pure, though considerable progress has been made towards its isolation.

Attention is directed to the attempts now being made to elucidate the arrangement of amino-acids within the protein molecules, attempts which seem likely to prove of increasing importance and value as methods continue to improve for characterising and estimating specific amino-acids and for synthesising more complex peptides.

The nature of the researches involved in chemotherapy makes material progress slow in this field. Nevertheless, results are emerging from prolonged systematic investigations and are making definite contributions to our knowledge of the mode of action, and of the relative efficiencies of both natural and synthetic therapeutic agents.

In the Plant Biochemistry section considerable space has been devoted this year to questions relating to photosynthesis in plants. Recent additions to our knowledge of the pure chemistry of chlorophyll[1] may contribute much to our understanding of the more physiological aspects of the photosynthetic process. The many ramifications of this problem and the divergence of opinion among authorities on this subject, coupled with the fact that nine years have elapsed since the matter was dealt with in these Reports, seem to afford sufficient justification for a general review of some of the more important researches and theories on this fundamental process of plant chemistry.

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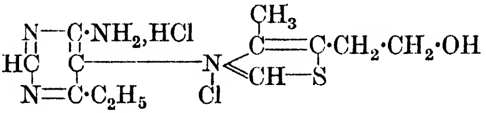
[1] *Ann. Reports*, **1935, 32, 362.**

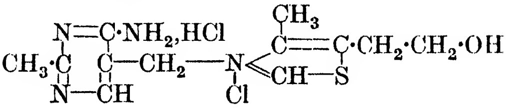
1. ANIMAL BIOCHEMISTRY.

The Vitamins.

Vitamin B_1.—The constitution of vitamin B_1 originally suggested by R. R. Williams (I) [1a] has been modified [2] to that shown in (II) and the new formula has been confirmed by synthesis.[3]



(I.)



(II.)

The excretion of vitamin B_1 in human urine has been measured by the bradycardia method,[4] the vitamin being first adsorbed on active clay, which is then fed to B_1-deficient rats for observation of its effect on the heart rate. Normally 12—35 international units (approximately 30—90 γ) are excreted per day, *i.e.*, about 5—8% of the daily intake. In human beri-beri the excretion of vitamin B_1 may almost cease, and a daily excretion of less than 12 units is held to indicate some deficiency of the vitamin in the diet. W. H. Schopfer [5] has estimated vitamin B_1 by measuring the amount of growth in the mould *Phycomyces Blakesleanus* on a vitamin-free synthetic medium after addition of vitamin concentrates; the method has, so far, however, only been applied successfully to fairly pure preparations.

On the grounds that many diseases showing anorexia, œdema (with consequent heart symptoms) and peripheral nerve degeneration (characteristic signs of experimental B_1-deficiency) may be due to a deficiency of the vitamin, and that in such cases the absorption of the vitamin from the intestine may be unsatisfactory, the parenteral administration of pure vitamin B_1 has been advocated by a number of workers. W. R. Russell [6] has obtained good results by this method in cases of chronic progressive neuritis, alcoholic neuritis, subacute combined degeneration of the spinal cord, etc., although in some of them oral administration had little or no effect.

[1a] *Ann. Reports*, 1935, **32**, 402.

[2] R. R. Williams, *J. Amer. Chem. Soc.*, 1936, **58**, 1063.

[3] This vol., p. 381.

[4] L. J. Harris and P. C. Leong, *Lancet*, 1936, **230**, 886.

[5] *Z. Vitaminforsch.*, 1935, **5**, 67.

[6] *Edin. Med. J.*, 1936, **43**, 315.

Vitamin B_2 Complex.—Although it has been suggested that the term B_2 should be restricted to lactoflavin,[7] there is still no uniformity in nomenclature, and since there evidently exist more than the two factors which led to the differentiation of the complex into B_2 (flavin) and B_6 (curative of rat dermatitis) the tendency is to refer to the factors by their effects rather than by specific names. T. W. Birch, P. György, and L. J. Harris [8] distinguish at least two and possibly four factors in addition to flavin. They find that the factor curative of dermatitis in rats (erroneously described as rat-pellagra) is present in considerable amounts in maize, and in molasses, so that rats fed on typical human-pellagra-producing diets remained free from dermatitis, and such diets cured rats suffering from dermatitis. They conclude that this factor ($= B_6$) is different from the factor curative of human pellagra. This, the " P–P " or pellagra-preventing factor, is found especially in liver extract, autolysed yeast, etc., and is apparently not required by the rat. It is not lactoflavin (which is required by the rat, of course, for growth). Dogs fed on a human-pellagra-producing diet did not develop pellagra, but " black tongue " (a condition unaffected, evidently, by B_6), which was cured by a diet rich in P–P factor but not by lactoflavin. The dog, however, needs B_6 as well as lactoflavin and the " anti-black tongue " factor, as was shown by experiments with " synthetic " diets. It seems that the black tongue and the P–P factor may be identical, though the evidence is not conclusive. Finally the factor curative of chicken pellagra is differentiated from B_6, though its relation to the P–P or the black tongue factor was not decided.

S. Lepkowsky and T. H. Jukes [9] found that the factor curing dermatitis in chickens could be concentrated from aqueous rice bran extracts, since inert matter, but not the vitamin, was absorbed by fullers' earth. Their experiments suggested that the factor (B_6) curative of rat dermatitis was absorbed by the earth, and later experiments [10] confirmed this.

T. H. Jukes and S. Lepkowsky [11] investigated the distribution of the anti-chicken-dermatitis factor in foodstuffs. They found, for example, that wheat germ, kale, and maize contained approximately equal amounts, and since wheat germ and kale contain much more of the P–P factor than does maize, they conclude that the two are different. They thus confirm the differentiation of the rat-dermatitis and the chick-dermatitis factor and show that the

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[7] *Ann. Reports*, 1935, **32**, 404.

[8] *Biochem. J.*, 1935, **29**, 2830.

[9] *J. Biol. Chem.*, 1936, **114**, 109.

[10] S. Lepkowsky, T. H. Jukes, and M. E. Krause, *ibid.*, 1936, **115**, 557.

[11] *Ibid.*, 1936, **114**, 117.

latter is different from the P–P factor. The vitamin B_2 complex, therefore, consists of, at least, four factors, including lactoflavin.

Concerning vitamin B_2 itself (*i.e.*, the flavin growth factor) R. Kuhn, H. Rudy, and F. Weygand [12] have now reported the synthesis, by a method which fixes the position of the phosphoric acid residue, of 6 : 7-dimethyl-9-*d*-riboflavin-5′-phosphoric acid, which is identical with the natural lactoflavin phosphoric acid in solubility of its salts, absorption spectrum, oxidation–reduction potential, and in growth-promoting activity (rats) whether given orally or intra-peritoneally. R. Kuhn and H. Rudy [13] have shown further that the synthetic can replace the natural substance in the "yellow enzyme." R. Kuhn, H. Rudy, and F. Weygand [14] have also synthesised the *l*-arabinose analogue, and have shown that it too can combine with the colloidal carrier derived from the yellow enzyme to form a chromoprotein whose catalytic activity is high, though less than that of the natural enzyme.

Vitamin B_4.—The existence of vitamin B_4, originally described by V. Reader,[15] has more recently been doubted, and the opinion expressed that vitamin B_4 deficiency (so-called) is merely a chronic deficiency of vitamin B_1, and can be cured by a sufficiently large dose of that substance.[8, 16] H. von Euler [17] states, however, that in his laboratory M. Malmberg was unable to restore growth in rats by addition to the diet of vitamin B_2 and lactoflavin. J. A. Keenan, O. L. Kline, C. A. Elvehjem, and E. B. Hart [18] found in 1933 that concentrates of the alleged vitamin B_4 were able to prevent the development of certain paralytic symptoms in the chick, the diet already containing adequate amounts of vitamin B_1. This work was later confirmed and extended.[19] Now,[20] it has been shown that by the use of specially purified diets, crystalline vitamin B_1, and highly potent liver concentrates as source of the vitamin B_2 complex, it is possible to reproduce in rats the syndrome described by Reader and to restore growth by vitamin B_4 concentrates (*e.g.*, from peanuts) but not by crystalline vitamin B_1. These workers

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[12] *Ber.*, 1936, **69**, 1543.

[13] *Ibid.*, p. 1974.

[14] *Ibid.*, p. 2034.

[15] *Biochem. J.*, 1929, **23**, 689; 1930, **24**, 77, 1827.

[16] J. R. O'Brien, *Chem. and Ind.*, 1934, **53**, 452; L. J. Harris, *Ann. Rev. Biochem.*, 1935, **4**, 331; H. W. Kinnersley, J. R. O'Brien, and R. A. Peters, *Biochem. J.*, 1935, **29**, 701.

[17] *Ann. Rev. Biochem.*, 1936, **5**, 364.

[18] *J. Biol. Chem.*, 1933, **103**, 671.

[19] O. L. Kline, O. D. Bird, C. A. Elvehjem, and E. B. Hart, *J. Nutrition*, 1936.

[20] O. L. Kline, C. A. Elvehjem, and E. B. Hart, *Biochem. J.*, 1936, **30**, 780.

consider, therefore, that vitamin B_4 is a real entity with demonstrable functions in at least two species of animals.

Vitamin C.—With the definite identification of vitamin C as ascorbic acid, interest has shifted to such questions as its synthesis *in vivo*, its excretion under various conditions, the form in which it occurs in the tissues, the changes it undergoes there, and its functions. The published results bearing on these questions are, in many cases, contradictory, largely in all probability because the usual methods for estimating ascorbic acid (titration with 2 : 6-dichlorophenolindophenol is the commonest) are by no means specific. Many of the published conclusions can, therefore, be accepted only with reserve.

The report of B. C. Guha and A. R. Ghosh,[21] that rat tissues were able to synthesise ascorbic acid *in vitro* from mannose, has been contradicted by R. Ammon and G. Grave [22] and by M. Laporta and E. Rinaldi.[23] On the other hand, *in vivo* synthesis of ascorbic acid by rats is suggested by the experiments of K. M. Daoud and M. A. S. El Ayadi [24] and evidence has been adduced in support of the view that the human fœtus [25] and the human suckling,[26] but not the guinea pig fœtus or suckling,[27] can synthesise the vitamin to some extent. It has also been suggested by H. K. Müller [28] that the eye lens is capable of synthesising ascorbic acid, but S. W. Johnston [29] finds that, although in scorbutic guinea pigs the indophenol-reducing power of the lens is merely reduced, the ascorbic acid determined spectrographically has completely disappeared from lens and humours, the rate of disappearance (and of re-appearance when the vitamin is administered) running parallel with that of the other tissues. On the other hand, it has been claimed [30] that the indophenol-reducing substance of the lens and eye humours is ascorbic acid, since it is completely oxidised by the ascorbic acid oxidising enzyme—a conclusion which is obviously not justified until more is known of the specificity of the enzyme. Other indophenol-reducing substances (besides those which, like

[21] *Ann. Reports*, 1935, **32**, 404.

[22] *Z. Vitaminforsch.*, 1936, **5**, 185.

[23] *Boll. Soc. ital. Biol. sperim.*, 1935, **10**, 319.

[24] *Biochem. J.*, 1936, **30**, 1280.

[25] R. Rohmer, N. Bezssonoff, and E. Storr, *Compt. rend. Soc. Biol.*, 1936, **121**, 987.

[26] *Idem, Bull. Acad. Méd.*, 1935, **113**, 669; *Compt. rend. Soc. Biol.*, 1936, **121**, 988.

[27] G. Mouriquand, A. Cœur, and P. Viennois, *Compt. rend. Soc. Biol.*, 1936, **121**, 1005.

[28] *Klin. Woch.*, 1935, **14**, 1498.

[29] *Biochem. J.*, 1936, **30**, 1430.

[30] L. Rosner and J. Bellows, *Proc. Soc. Exp. Biol. Med.*, 1936, **34**, 493.

cysteine, reduce it slowly) do exist in nature, for one containing nitrogen, and possibly phosphorus, has been obtained from suprarenals by E. Ott, K. Kramer, and W. Faust.[31]

A similar confusion exists on the question of the state in which ascorbic acid exists in the tissues. Thus B. C. Guha and J. C. Pal,[32] having found that some plant extracts (*e.g.*, cabbage) yielded more ascorbic acid on heating, concluded that ascorbic acid was present to some extent in a combined form, whereas G. L. Mack[33] and M. van Eekelen[34] attribute the phenomenon to heat-inactivation of the ascorbic acid oxidase. Van Eekelen considers that an analogous phenomenon occurs in blood, ascorbic acid being oxidised by the erythrocytes, but A. E. Kellie and S. S. Zilva[35] deny that intact erythrocytes are capable of oxidising ascorbic acid. By spectrographic measurement they conclude that plasma contains no dehydroascorbic acid.

A large number of papers deal with the urinary excretion of ascorbic acid, and many are concerned with the unsatisfactory nature of the available methods. M. A. Abbasy, L. J. Harris, S. N. Ray, and J. R. Marrack,[36] using the method described by L. J. Harris and S. N. Ray,[37] state that the urinary excretion of ascorbic acid is, in general, proportional to the intake, and for normal adults (in England) receiving small allowances of fruit, etc., is about 20 mg. per day. A diet is deficient in vitamin C when the urinary output falls below 10—15 mg. per day (per 10 stone body weight) or when a dose of 700 mg. of ascorbic acid produces no increased excretion on the second day. The increased indophenol-reducing power of the urine after ascorbic acid administration, and the decrease during the feeding of a scurvy-producing diet, which has been observed by others as well as Harris and his co-workers, certainly suggest that the reducing substance of urine is ascorbic acid or at least a closely related substance. B. Ahmad[38] found that a high meat diet caused a very considerable increase in the excretion of indophenol-reducing substance, and concluded that this was probably ascorbic acid from a study of its heat stability. A failure to detect ascorbic acid by biological assay he ascribed to the presence of toxic substances in urine. Wieters[39] also has failed to demonstrate ascorbic acid in urine by biological methods. Although these failures can be discounted to some extent by accepting Ahmad's explanation, it is more difficult to ignore the

[31] *Z. physiol. Chem.*, 1935, **243**, 199.

[32] *Nature*, 1936, **137**, 946.

[33] *Ibid.*, 1936, **138**, 505.

[34] *Acta Brev. Néerl.*, 1935, **5**, 78.

[35] *Biochem. J.*, 1936, **30**, 361.

[36] *Lancet*, 1935, **229**, 1399.

[37] *Ibid.*, p. 71.

[38] *Biochem. J.*, 1936, **30**, 11.

[39] *Mercks Jahresber.*, 1935.

chemical results reported by K. Hinsberg and R. Ammon.[40] They were able to separate from urine ascorbic acid added to the extent of 1 mg. per 100 c.c., using the fact that its derivative with 2 : 4-dinitrophenylhydrazine is insoluble in cold alcohol or in ethyl hydrogen oxalate but soluble in ethyl oxalate. From normal urine (containing more than this amount of indophenol-reducing substance) they failed to extract any of the vitamin C derivative, and from a study of the limits of their methods conclude that normal urine cannot contain more than 0·3 mg. of ascorbic acid per 100 c.c.

The fact that ascorbic acid exists in the tissues largely, if not entirely, in the reduced form has been ascribed by several authors to the presence of glutathione,[41] which has also been shown to protect ascorbic acid from autoxidation *in vitro*, provided that it is present in relatively large amounts.[42] It is claimed that in high concentration, glutathione can even reduce dehydroascorbic acid, provided the p_H is not too low.[43] F. G. Hopkins and E. J. Morgan [44] have studied the relationship between ascorbic acid and glutathione, alone and in the presence of the enzyme (from cauliflower, cabbage, etc.) which A. Szent-Györgi [45] found to oxidise ascorbic acid and named "hexoxidase." They find that a mixture of pure ascorbic acid with pure glutathione may be quite inert, neither being oxidised (*e.g.*, at p_H 6); if, however, a trace of copper is present and the p_H is such as to allow oxidation of the glutathione (*e.g.*, 7·4), the former is protected while the latter is oxidised exactly as if no ascorbic acid was present. They are, therefore, inclined to ascribe the protective action of glutathione under these conditions to its formation of a stable compound with the metal catalyst. In the presence of the enzyme the conditions are quite different.

The reactions

$$\text{Ascorbic acid} \longrightarrow \text{dehydroascorbic acid}$$
$$\text{Dehydroascorbic acid} + 2\text{GSH} \longrightarrow \text{ascorbic acid} + \text{G·S·S·G}$$

are both catalysed by the enzyme, and, the second of these being the more rapid, ascorbic acid remains practically fully reduced until all the glutathione is oxidised. Hopkins and Morgan point out that so far no enzyme capable of oxidising either ascorbic acid or glutathione has been discovered in animal tissues. Nevertheless,

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[40] *Biochem. Z.*, 1936, **288**, 102.

[41] L. de Caro and M. Giani, *Z. physiol. Chem.*, 1934, **228**, 13; C. A. Mawson, *Biochem. J.*, 1935, **29**, 569.

[42] Bersin, Koster, and Zusatz, *Z. physiol. Chem.*, 1935, **235**, 12.

[43] H. Borsook and C. E. P. Jeffreys, *Science*, 1936, **83**, 397.

[44] *Biochem. J.*, 1936, **30**, 1446.

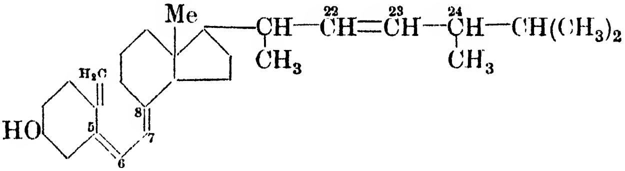
[45] *Ibid.*, 1928, **22**, 1387.

their experiments in which these substances were aerated with hepatic tissue yielded some suggestion that here too glutathione affords some protection to the vitamin. Other substances besides glutathione may well be concerned in preserving ascorbic acid from oxidation; for instance, M. Yamomoto[46] has shown adrenalin to have this effect *in vitro.*

S. Rusznyak and A. Szent-Györgi[47] report that Hungarian red pepper and lemon juice contain a substance which is closely allied to vitamin C, curing pathological fragility and permeability of the capillary walls to plasma proteins. They name it vitamin P, and state that it appears to be flavone or flavonol glucoside.

Vitamin D.—The fact that antirachitic activity is the property of more than one compound was mentioned in these Reports last year.[48] During the year under review the number of active substances has been increased, and for the first time one has been isolated from natural sources. The evidence leading to the accepted constitution of these compounds is reviewed elsewhere:[49] it is believed that all the active substances so far obtained have in common the three-ring structure with the three conjugated double bonds of calciferol (III).[50]

(III.)



A. Windaus[48, 51] found, over a year ago, that 7-dehydrocholesterol, differing from ergosterol in having no double bond at C_{22}–C_{23} and no methyl group at C_{24}, but with the same ring structure, yielded an antirachitic substance on irradiation. He has now, with F. Schenk and F. von Werder,[52] succeeded in isolating the irradiation product (vitamin D_3) by chromatographic absorption on alumina. It has an activity of 24,000 international units per mg. (*i.e.*, rather more than half that of calciferol). H. Brockmann[53] has isolated a compound identical with vitamin D_3, from tunny liver oil, and various experiments on the relative effects of different

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[46] *Z. physiol. Chem.*, 1935, **243**, 266.

[47] *Nature*, 1936, **138**, 27.

[48] *Ann. Reports*, 1935, **32**, 405.

[49] This vol., p. 349.

[50] I. M. Heilbron, R. N. Jones, K. M. Samant, and F. S. Spring, *J.*, 1936, 905.

[51] A. Windaus, H. Lettré, and F. Schenk, *Annalen*, 1935, **520**, 98.

[52] *Z. physiol. Chem.*, 1936, **241**, 100.

[53] *Ibid.*, p. 104.

liver oils in curing avian rickets suggest that it is present in other fish liver oils (*e.g.*, those of cod and halibut) as well.[54] G. A. D. Haslewood and J. C. Drummond [55] also have obtained a highly active concentrate from tunny liver oil (10,000—20,000 international units per mg.), but believe it to be different from the vitamin D_3 of Brockmann and Windaus.

That calciferol is much less effective in curing avian rickets than an amount of cod liver oil containing an equal number of international (rat) units of vitamin D has been mentioned in these Reports before.[48] It has also been found that purified cholesterol, apparently free from ergosterol, still possesses provitamin D properties. Cholesterol purified through the dibromide is only slightly active, but its activity (or rather activatability) is greatly increased if it is heated in presence of a little oxygen.[56, 57] The irradiation products of crude cholesterol and of purified heated cholesterol resemble cod liver oil in their efficacy in avian rickets.[57] A. G. Boer, E. H. Reerink, A. Van Wijk, and J. van Niekerk [58] have isolated the provitamin from crude cholesterol, confirmed the activity of its irradiation product as resembling that of cod liver oil with respect to avian rickets, and identified it as 7-dehydrocholesterol. The suggestion arises, therefore, that purified cholesterol may, under the conditions used by M. L. Hathaway and D. E. Lobb,[57] undergo dehydrogenation to a small extent. Since irradiated plant products (cottonseed oil, wheat middlings, lucerne leafmeal, yeast, fungus mycelium) resemble calciferol in being much more efficacious in rat than in avian rickets, it has been suggested that plant and animal fats contain different vitamin D precursors.[59] The similarity in this respect between the unsaponifiable matter from lucerne oil and calciferol is confirmed by A. Black and H. L. Sasaman,[54] who extend the similarity to irradiated " phytosterol." It is possible, of course, that crude phytosterols, like crude cholesterol, may contain small amounts of dehydro-derivatives, for O. Linsert [60] has prepared 7-dehydrostigmasterol, which on irradiation shows definite antirachitic activity, as does 7-dehydrosito-

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[54] M. J. L. Dols, *Z. Vitaminforsch.*, 1936, **5**, 161; A. Black and H. L. Sassaman, *Amer. J. Pharm.*, 1936, **108**, 237.

[55] *Chem. and Ind.*, 1936, 598.

[56] C. E. Bills, E. M. Honeywell, and W. A. MacNair, *J. Biol. Chem.*, 1928, **76**, 251; J. Waddell, *ibid.*, 1934, **105**, 711; M. L. Hathaway and F. C. Koch, *ibid.*, 1935, **108**, 773.

[57] *Ibid.*, 1936, **113**, 105.

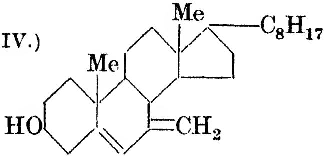
[58] *Proc. K. Akad. Wetensch. Amsterdam*, 1936, **39**, 662.

[59] R. M. Bethke, P. R. Record, and O. H. M. Wilder, *J. Biol. Chem.*, 1935, **112**, 231.

[60] *Z. physiol. Chem.*, 1936, **241**, 125.

sterol, which has been prepared by W. Wunderlich.[61] The irradiation products of these substances have not yet been isolated, so their activity has not been measured quantitatively. It is interesting to note that, again, the power of acquiring antirachitic activity is associated with the ring structure found in cholesterol, but that again the side chain is of little importance, for whereas stigmasterol has the unsaturated side chain of ergosterol with, however, an ethyl group at C_{24}, sitosterol has the ethyl group at C_{24} but a saturated side chain. The relative unimportance of the side chain is further shown by the fact that 22-dihydroergosterol becomes antirachitic on irradiation.[48, 62] The presence of two conjugated double bonds in the ring structure is important, and that they must be in the ring itself is suggested by the inactivity after irradiation of 7-methylenecholesterol (IV) prepared by B. Bann, I. M. Heilbron, and F. S. Spring.[63]

(IV.)



Vitamin E.—From the unsaponifiable fraction of wheat germ oil, H. M. Evans, O. H. Emerson, and G. A. Emerson [64] have isolated a substance believed to be the allophanate of β-amyrin, the allophanate of an alcohol, $C_{29}H_{50}O_2$, and the allophanate of " α-tocopherol," $C_{29}H_{50}O_2$. The alcohol from the first of these is inactive, the second shows some vitamin E activity, but a single 3 mg. dose of the regenerated α-tocopherol regularly enables vitamin E deficient rats to bear young. A dose of 1 mg., however, was insufficient to allow the regular production of litters. α-Tocopherol (*tokos*, childbirth, and *phero*, to bear) is an apparently homogeneous, oily alcohol, optically inactive, with a strong absorption band maximal at 2980 A. The relatively inactive alcohol has similar absorption, which appears to explain the observation of H. S. Olcott [65] that certain concentrates with good absorption at 2940 A. showed little or no vitamin activity. Treatment of α-tocopherol with silver nitrate in methyl alcohol caused the disappearance of the absorption band at 2980 A., with appearance of two new bands at 2710 and 2620 A., the biological activity being reduced but not lost. (Drummond *et al.*[66] have stressed the presence of absorption at 2670 A. as well as 2940 A. in their active concentrates.) Ollcott

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[61] *Z. physiol. Chem.*, 1936, **241**, 116.

[62] A. Windaus and R. Langer, *Annalen*, 1933, **508**, 105; F. G. McDonald, *Proc. Amer. Soc. Biol. Chem.* (*J. Biol. Chem.*), 1936, **114**, lxv.

[63] *J.*, 1936, 1274.

[64] *J. Biol. Chem.*, 1936, **113**, 319.

[65] *Ibid.*, 1935, **110**, 695.

[66] *Biochem. J.*, 1935, **29**, 2510.

(*loc. cit.*) had observed the similar persistence of activity with disappearance of the absorption band at 2940 A. when his concentrates were treated with methyl-alcoholic silver nitrate, but concluded that the substance responsible for the absorption was, therefore, not the vitamin. A similar conclusion has been reached by J. C. Drummond, E. Singer, and R. J. MacWalter,[66] who found certain preparations to be less active than was expected from the absorption intensity, although they had earlier [67] believed absorption and activity to be parallel. They point out, however, that the band at 2940 A. may really be characteristic of the vitamin, but that certain molecular changes may affect potency without affecting the absorption spectrum. Evans and his collaborators, however, consider that the effect of silver nitrate merely shows provitamin E activity to be possessed by more than one substance, since (on the basis of its conversion into a *p*-nitrophenylurethane derivative and regeneration unchanged, as well as the failure to effect any fractionation by solvents or adsorption on a calcium carbonate column) they consider α-tocopherol to be a chemical individual.

The most potent preparations of Drummond gave analytical data, for both the free alcohol and its acetate, in good agreement with those for α-tocopherol. R. H. Kimm [68] also has obtained a highly active substance which, from analysis of its β-naphthoate, appears to have the formula $C_{29}H_{48}O$. This is, of course, the formula of tocopherol *minus* H_2O, but the published chemical data are too scanty to permit reasoned suggestions as to the relationship of the two substances. All that is known is that tocopherol is an alcohol, yielding a monoallophanate and a mono-*p*-nitrophenylurethane, that it does not react with ketone reagents, that it probably contains a condensed cyclic nucleus, and that it contains reactive ethylenic linkages.

The suggestion that vitamin E is required for growth as well as fertility is negatived by experiments [69] in which the growth of rats was measured from weaning on a diet free from E but otherwise adequate. The growth was as good as that of rats on a stock colony diet and was accelerated only very slightly in males (but not in females) when vitamin E concentrates were used to supplement the basic diet. Small supplements of wheat germ oil, sufficient to ensure fertility, were without effect on growth. The inclusion of lard, however (the fat in the basic diet consisted of the ethyl esters of fatty acids from hydrogenated cotton seed oil), produced

[67] *Biochem. J.*, 1935, **29**, 456.

[68] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **28**, 74.

[69] H. S. Olcott and H. A. Mattill, *Proc. Amer. Soc. Biol. Chem.* (*J. Biol. Chem.*), 1936, **114**, lxxvii.

a significant increase in the growth rate, a fact of some interest in view of the suggestion that certain unsaturated fatty acids are essential dietary constituents.

Vitamin K.—H. Dam and F. Schønheyder [70] described, in 1934, a deficiency disease in chicks, characterised by a tendency to hæmorrhage, anæmia, pathological changes in the gizzard, and a prolonged blood clotting time. This was later [71] ascribed to lack of a specific fat-soluble, thermostable vitamin (K) and the suggestion was confirmed independently by H. J. Almquist and E. L. R. Stokstad.[72] The vitamin occurs in hog's liver fat (one of the first sources) and to a smaller extent in dog, chick, and cod liver; green vegetables are a particularly rich source.[73] The vitamin is destroyed by alkali.[73, 74] H. Dam and F. Schønheyder [73] have achieved a partial purification from alfalfa by extraction with various solvents, followed by adsorption on calcium carbonate or cane sugar, their most active preparation containing 600 to 1000 units per mg. (A unit is defined [75] as the smallest daily dose per g. body weight which, given for three days, will restore the clotting time to normal. Thus a chick weighing 400 g. would require 1200 units.) H. J. Almquist,[74] also by solvent fractionation from alfalfa, obtained a concentrate of which 2 mg. were adequate when added to 1 kg. of vitamin-free diet; later [76] by fractional distillation in a vacuum he obtained a yellow viscous oil of which 0·5 mg. per kg. of diet was adequate. Exact comparison of the degree of concentration achieved by the two workers is not possible in the absence of data as to weight of chicks and food consumption in Almquist's experiments, though it seems likely that his preparation is the more active. As to the mode of action of vitamin K, F. Schønheyder [77] has suggested, and H. Dam, F. Schønheyder, and E. Tage-Hansen [78] support the view, that the low clotting power in the blood of chicks lacking the vitamin is due to a reduced pro-thrombin content. Treatment of the serum from normal chicks by the methods of Howell or Mellanby gives precipitates with pro-thrombin activity, though serum from K-avitaminous chicks, treated similarly, gives inactive precipitates. Vitamin K concentrates themselves, however, do not accelerate clotting *in vitro*, but pro-thrombin from

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[70] *Biochem. J.*, 1934, **28**, 1935.
[71] *Nature*, 1935, **135**, 653; *Biochem. J.*, 1935, **29**, 1273.
[72] *J. Biol. Chem.*, 1935, **111**, 105.
[73] *Biochem. J.*, 1936, **30**, 897.
[74] *J. Biol. Chem.*, 1936, **114**, 241.
[75] *Biochem. J.*, 1936, **30**, 890.
[76] *J. Biol. Chem.*, 1936, **115**, 589.
[77] *Nature*, 1935, **135**, 652.
[78] *Biochem. J.*, 1936, **30**, 1075.

normal chick serum, extracted with acetone and ether to remove lipoids, itself exhibits vitamin K activity. It is possible that the vitamin may be present in pro-thrombin as a prosthetic group in definite chemical combination with the rest of the molecule.

Hormones.

Adrenal Cortex.—Recent work has shown the nucleus of the sex hormones, of the sterols, the bile acids, the cardiac aglucones, and the antirachitic vitamin to be present in yet another substance of biological importance.

The necessity for life of a substance produced by the adrenal cortex was shown in the case of adrenalectomised dogs by J. M. Rogoff and G. N. Stewart,[79] who later [80] found that their extracts were of some benefit in cases of Addison's disease. Similar results were obtained by W. W. Swingle and J. J. Pfiffner,[81] and by F. A. Hartman.[82] The hormone preparations used by these workers were very impure, but in 1934 the isolation of a crystalline substance having the activity of the cortical hormone was announced from the Mayo Clinic.[83] The crystals were later found to be a mixture,[84] but recently H. L. Mason, C. S. Myers, and E. C. Kendall [85] have separated from a number of somewhat similar compounds one which has definite, though small, activity when tested on the rat. It is described as a strongly dextrorotatory, unsaturated ketonic alcohol, $C_{21}H_{30}O_5$, m. p. 201—208°.

The fact that this preparation is less active than was expected suggested that it is still impure, and certainly its description does not tally with that of an active substance obtained by Reichstein. Early in 1936 T. Reichstein [86] reported the ready concentration of the cortical hormone by means of ketonic reagents after preliminary treatment with pentane and 20% methyl alcohol. From these active concentrates (and in part from inactive by-products) he obtained nine crystalline substances, all apparently closely related. One of these substances, β-*adrenosterone*, has one-fifth of the activity of androsterone by the capon test, three more are oxidisable to substances with slight androsterone-like activity, a fifth is oxidised

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[79] *Amer. J. Physiol.*, 1928, **84**, 660.

[80] *J. Amer. Med. Assoc.*, 1929, **92**, 1569.

[81] *Science*, 1930, **71**, 321.

[82] *Endocrinology*, 1930, **14**, 229.

[83] E. C. Kendall, H. L. Mason, B. F. McKenzie, C. S. Myers, and G. A. Koelsche, *Proc. Staff Meetings, Mayo Clinic*, 1934, **2**, 245.

[84] E. C. Kendall, *J. Amer. Med. Assoc.*, 1935, **105**, 1486.

[85] *J. Biol. Chem.*, 1936, **114**, 613.

[86] *Helv. Chim. Acta*, 1936, **19**, 29, 223, 402, 979, 1107.

to adrenosterone and is considered, though without cortical activity, to be identical with the active substance of Kendall *et al.* If this identification is correct, it follows that the preparation obtained by Kendall and his collaborators is a mixture containing a small amount of the hormone. Of the nine substances obtained by Reichstein, eight were devoid of cortical activity when tested on rats by the Everse–de Fremeny [87] method in doses of 0·5—2 mg. The ninth has recently [88] been found to be active, and to yield on further fractionation a pure crystalline compound, m. p. 180—182°, which "shows to a large extent the biological activity of the raw material," and is named *corticosterone*. By the method of Everse and de Fremeny, 0·5—1 mg. represents the approximate rat unit; tested on dogs, 0·25—0·5 mg. of corticosterone was found to be equivalent to 1 c.c. of standard "cortin" solution. It is claimed that the chemical formula, with the exception of a few details, has been elucidated. It has not yet been reported, but the impure substance of which corticosterone is the main constituent was described as an $\alpha\beta$-unsaturated ketone. Reichstein and his co-workers point out that the isolation of corticosterone does not exclude the possibility that other active or activating substances may be present in the gland.

Insulin.—From the results of electrometric titration of crystalline insulin, C. R. Harington and A. Neuberger [89] have deduced that the insulin molecule contains 43 ± 2 acid-binding groups and 60—70 base-binding groups. A study of iodinated insulin suggests that in iodination only the tyrosine groups are affected (substituted in the 3 : 5-positions) and on this assumption it appears that the insulin molecule contains 24 tyrosine molecules. Titration of the iodinated protein suggests that the phenolic groups are free in insulin. Since iodinated insulin is almost inactive physiologically and activity is (nearly) proportionately restored by partial removal of the iodine, it seems that the phenolic groups of insulin are important in relation to its physiological activity. Combining these results with an estimate of the amide nitrogen of insulin (34 groups per mol.), C. R. Harington and T. H. Mead [90] have shown that insulin contains about 30% of glutamic acid. In view of inactivation which follows release of the labile amide nitrogen or the labile sulphur from insulin and of the suggestion that insulin may contain a "prosthetic group" just as thyreoglobulin owes its

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[87] J. W. Everse and P. de Fremeny, *Acta Brev. Néerl.*, 1932, **2**, 152.

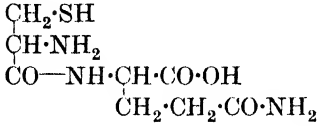
[88] P. de Fremeny, E. Laqueur, T. Reichstein, R. W. Spanhoff, and I. E. Uyldert, *Nature*, 1937, **139**, 26.

[89] *Biochem. J.*, 1936, **30**, 809.

[90] *Ibid.*, p. 1598.

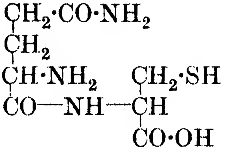
activity to thyroxin, Harington and Mead have synthesised cysteylglutamine (V) and glutaminyl-cysteine (VI).

(V.)



$$\begin{array}{ll}\mathrm{CH_2{\cdot}SH} & \\ \mathrm{CH{\cdot}NH_2} & \\ \mathrm{CO{-}NH{\cdot}} & \mathrm{CH{\cdot}CO{\cdot}OH} \\ & \mathrm{CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2}\end{array}$$

(VI.)



$$\begin{array}{ll}\mathrm{CH_2{\cdot}CO{\cdot}NH_2} & \\ \mathrm{CH_2} & \\ \mathrm{CH{\cdot}NH_2} & \mathrm{CH_2{\cdot}SH} \\ \mathrm{CO{-}NH{-}} & \mathrm{CH} \\ & \mathrm{CO{\cdot}OH}\end{array}$$

Both of these peptides were, however, without hypoglycæmic effect in the disulphide as well as the sulphydryl form. The lability of their amide nitrogen was not far removed from that of insulin; their sulphur, however, was far less labile.

An interesting development in the therapeutic use of insulin is due to H. C. Hagedorn, B. N. Jensen, N. M. Krarup, and I. Wudstrup,[91] who find that insulin combines with protamines to form complexes which have isoelectric points at about p_{H} 7·3, at which they are only slightly soluble in water though rather more so in serum. Their low solubility results, after their subcutaneous injection, in the slow absorption of insulin into the body fluids. In consequence, the hypoglycæmic effect of an injection of protamine insulinate lasts about twice as long as that of the same amount of free insulin. These results have been confirmed repeatedly,[92] and it has been shown that (in rabbits) protamine insulinate could be detected in the lymphatics five hours after injection, whereas ordinary insulin had disappeared in 45 minutes.[93] The published data, however, indicate that there is, as yet, no general agreement as to the best way of using the new modification of insulin therapy. Indeed, it seems likely that not only will different types of diet demand rather different ways of using standard insulin along with protamine insulinate, but that by using, *e.g.*, different protamines it may be possible to produce complexes suited to particular purposes.

The Sex Hormones.—The chemical relationships of the numerous active substances which have recently been obtained are discussed elsewhere in this volume.[94]

D. W. McCorquodale, S. A. Thayer, and E. A. Doisy [95] have isolated dihydrotheelin (= oestradiol) from sow ovaries and have found it to be identical in melting point and biological assay with

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[91] *J. Amer. Med. Assoc.*, 1936, **106**, 177.

[92] *E.g.*, H. W. Boolt *et al.*, *ibid.*, p. 180; R. D. Lawrence and N. Archer, *Brit. Med. J.*, 1936, i, 747; I. M. Rabinowitch *et al.*, *Canadian Med. Assoc. J.*, 1936, **35**, 124.

[93] H. K. Beecher and A. Krogh, *Nature*, 1936, **137**, 458.

[94] P. 356.

[95] *Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 1182.

the substance obtained by catalytic hydrogenation of oestrone. An improved method of isolation from the aspirated liquor folliculi—as the di-α-naphthoate—leads to the conclusion [96] that at least 52% of the oestrogenic activity of the starting material is due to dihydrotheelin, which, therefore, is the chief active principle of the sow's ovary (though others may be present). The amount present is about 0·015 mg. per kg. of ovary. Two isomeric dihydrotheelins have been isolated from the urine of pregnant mares.[97] The two isomers should both be obtained by chemical reduction of oestrone, and McCorquodale's material, therefore, is a mixture or the two isomers have equal activities.

R. H. Andrew and F. Fenger [98, 99] have reported the isolation from ovaries of a substance, probably $C_{20}H_{41}O_2N$, of which 0·00001 mg. produces oestrus in rats after 96 hours. This would appear to be the most active oestrogenic substance yet obtained.

The existence in pregnancy urine of bound oestrogenic material liberated by boiling with hydrochloric acid has been confirmed by G. van S. Smith and O. W. Smith.[1] S. L. Cohen and G. F. Marrian [2] have obtained from pregnancy urine a water-soluble, ether-insoluble, amorphous substance containing about 50% of its weight of oestriol. Its composition and reactions suggest that it is a compound of oestriol and glycuronic acid, a suggestion which has been confirmed by later work.[3]

Testosterone remains the most active male hormone from natural sources, though its 17-methyl ether is stated to be more active in the capon test and also, incidentally, to possess progesterone activity [4] (the two compounds are R–O–Me and R–CO–Me, respectively). The activity of testosterone is said to be increased by increase in the amount of the oily medium in which it is administered [5] or by esterification with acetic or propionic acid.[6] Possibly by these means it is protected from destruction in the animal body. Like some of the artificial male hormones (particularly those containing ethylenic linkages), both androsterone and testosterone are described as possessing certain of the properties of the ovarian

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[96] *J. Biol. Chem.*, 1936, **115**, 435.

[97] *Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 1187.

[98] *Science*, 1936, **84**, 18.

[99] *Endocrinology*, 1936, **20**, 563.

[1] *Amer. J. Physiol.*, 1935, **112**, 340.

[2] *Biochem. J.*, 1936, **30**, 57.

[3] S. L. Cohen, G. F. Marrian, and A. D. Odell, *Biochem. J.*, 1936, **30**, 2250.

[4] L. Ruzicka and H. R. Rosenberg, *Helv. Chim. Acta*, 1936, **19**, 357.

[5] R. Deanesly and A. S. Parkes, *Lancet*, 1936, **230**, 837.

[6] A. S. Parkes, *ibid.*, 1936, **321**, 674.

hormones.[7] V. Korenchevsky, M. Dennison, and S. L. Simpson [8] have found in prolonged experiments that large doses of androsterone (or better androstanediol) caused a partial recovery of the atrophied uterus and vagina in sprayed rats. The administration of androsterone together with oestrone was more effective (especially in the recovery of the uterus) than either male or female hormone alone. A similar, though smaller, co-operation between androsterone and oestrone was shown in the rate of involution of the thymus, but the two substances appeared to antagonise each other in their effects on the adrenals (in which androsterone normally causes reduction of weight to normal) and on the body weight. A similar co-operative effect of the two hormones was also shown in the recovery of the sexual organs (and thymus) of males. As the authors point out, the mutual interaction of the male and female hormones is of considerable importance, since it is well established that both are found in normal urine from males and females. These experiments have been extended to testosterone and oestradiol.[9] Testosterone shows the same co-operative and antagonistic effects with the ovarian hormones as does androsterone, the action again being much more marked in females than in males. Testosterone (and also androstanediol), it is remarked, differs from androsterone in bringing about a *quantitatively* normal development of the male sexual organs, and these substances also produce some of the changes associated with progesterone. If, therefore, they are injected simultaneously with oestrone, the effects in females simulate some of those seen during pregnancy. Although in castrated male rats the effect of androsterone is increased by oestrone, the increase is not nearly so great as that produced by the " X " substance of Laqueur *et al.*, a substance, itself inert, obtained (impure) in extracts of plant or animal tissues.[10]

Proteins and Amino-acids.

Protein Structures.—Steady improvement in the methods available for the determination of individual amino-acids in protein hydrolysates is beginning to reveal stoicheiometrical relationships. Thus M. Bergmann [11] has extended his work on gelatin reported

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[7] E. Wolff and A. Ginglinger, *Compt. rend. Soc. Biol.*, 1936, **121**, 1476; E. Wolff, *ibid.*, p. 1474, V. Korenchevsky, *Nature*, 1936, **137**, 494; A. Butenandt, *Naturwiss.*, 1936, **24**, 16.

[8] *Biochem. J.*, 1935, **29**, 2534.

[9] V. Korenchevsky, M. Dennison, and I. Brovsin, *ibid.*, 1936, **30**, 558.

[10] *Acta Brev. Néer.*, 1935, **5**, 84; J. Freud, *ibid.*, p. 97; L. Ruzicka, M. W. Goldberg, and H. R. Rosenberg, *Helv. Chim. Acta*, 1935, **18**, 1487.

[11] M. Bergman and C. Niemann, *J. Biol. Chem.*, 1936, **115**, 77.

last year.[12] He finds that glycine, proline, hydroxyproline, arginine, alanine, leucine-*iso*leucine, and lysine occur in the molecular proportions 24 : 12 : 8 : 4 : 8 : 4 : 3. On the assumption of a regular arrangement of the amino-acids in a polypeptide chain this gives a periodicity (in the same order) of 3, 6, 9, 18, 9, 18, 24 and it is pointed out that these numbers are all multiples of 3. This periodicity of the amino-acids would be satisfied by either of the arrangements :

G–P–X–G–X–X–G–P–X–G– or G–X–P–G–X–X–G–X–P–G–

W. Grassmann and K. Riederle[13] have isolated lysylprolylglycine from gelatin, and since the first of Bergmann's suggested arrangements demands the presence only of glycylproline peptides, this supports the second. A similarly extensive stoicheiometrical relationship has been found among the amino-acids of blood fibrin (cattle), where glutamic acid, lysine, arginine, aspartic aid, proline, tryptophan, histidine, methionine, and cysteine (total 54·5% of the protein) are found to be in the molecular proportions 72 : 48 : 32 : 32 : 32 : 18 : 12 : 12 : 9, with corresponding periodicities 8, 12, 18, 18, 18, 32, 48, 48, 64.

Similarly, R. Block and H. Vickery[14] showed some years ago that the keratins form a group of proteins with histidine : lysine : arginine molecular ratios of 1 : 4 : 12. More recently, R. Block[15] has found that hæmoglobins exhibit another characteristic arrangement with iron : arginine : histidine : lysine in the ratios 1 : 3 : 8 : 9.

Another example of attempts to gain an insight into the structure of protein is supplied by H. Bauer and E. Strauss,[16] who, from a study of iodination of globin and various derivatives, have reached the conclusion that globin is a complex of six units, each of molecular weight 11,680, the units being linked through the glyoxaline groups of histidine.

Canavanine and Canaline.—M. Kitagawa and A. Takani[17] have confirmed the structure of canaline as $NH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$. By treatment of α-benzoylcanaline with methyl*iso*carbamide they obtained α-benzoylcanavanine, which yielded canavanine on hydrolysis. Canavanine is, therefore, confirmed as

$$NH_2{\cdot}C(\colon NH){\cdot}NH{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

the two amino-acids having the same relationship to each other as ornithine and arginine in conformity with the demonstration that

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[12] *Ann. Reports*, 1935, **32**, 418.

[13] *Biochem. Z.*, 1936, **284**, 177.

[14] *J. Biol. Chem.*, 1931, **93**, 113.

[15] *Ibid.*, 1934, **105**, 663.

[16] *Biochem. Z.*, 1936, **284**, 197, 231.

[17] *J. Agric. Chem. Soc. Japan*, 1935, **11**, 1077; *J. Biochem. Japan*, 1936, **23**, 181.

they can share in the synthesis of urea.[18] Incubation of canavanine with a pig liver extract at 37° yields canaline and γ-ethylidene-canaline, which can be hydrogenated to an α-amino-γ-hydroxy-acid, $C_4H_9O_3N$, and can be obtained from canaline and acetaldehyde.[19]

The growth-promoting action of canavanine, shown by M. Ogawa,[20] is denied by M. Kitagawa and M. Wada.[21] M. Ogawa [22] now states that canavanine is not essential for growth in the later part of the growing period and that it is beneficial to the health of pregnant animals though not essential for pregnancy.[23]

α-Amino-β-hydroxybutyric Acid.—In the course of feeding experiments with pure amino-acids, W. C. Rose [24] found that young rats failed to maintain themselves when supplied with a mixture of nineteen amino-acids instead of protein. Growth, however, occurred if the mixture was supplemented by a concentrate of the monamino-fraction of a protein hydrolysate. M. Womack and W. C. Rose [25] found that the supplementary concentrate supplied two factors, one of which was identified as *iso*leucine (which was present in the artificial mixture, but, evidently, in insufficient amount). The second essential factor has been isolated [26] from fibrin and shown to be α-amino-β-hydroxybutyric acid, since on reduction it gives α-aminobutyric acid, and since (unlike α-amino-γ-hydroxybutyric acid) it does not yield a lactone when warmed in acid solution. Moreover, α-amino-γ-hydroxybutyric acid (synthetic) was unable to replace the natural acid in growth experiments. H. E. Carter [27] prepared α-amino-β-hydroxybutyric acid by the method of E. Abderhalden and K. Heyns,[28] but the product was without effect in growth experiments. The synthetic material, obtained from crotonic acid, contained two of the four possible isomers. Carter, therefore, converted it into a mixture of the two epimers by preparing the formyl derivative, heating this with sodium hydroxide and acetic anhydride, and hydrolysing the product with hydrobromic acid. This treatment yielded a mixture which supported growth, with about a fifth of the activity shown by the natural acid. Attempts to con-

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[18] M. Kitagawa and T. Tomita, *Proc. Imp. Acad. Tokyo*, 1929, **5**, 380.

[19] M. Kitagawa, K. Sawada, and Y. Hosoki, *J. Agric. Chem. Soc. Japan*, 1935, **11**, 539.

[20] *Ibid.*, p. 558.

[21] *J. Agric. Chem. Soc. Japan*, 1935, **11**, 1083.

[22] *Ibid.*, 1936, **12**, 256.

[23] *Ibid.*, p. 828.

[24] *J. Biol. Chem.*, 1931–2, **94**, 155; C. T. Caldwell and W. C. Rose, *ibid.*, 1934, **107**, 57.

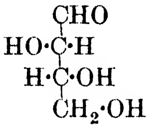
[25] *Ibid.*, 1935, **112**, 275.

[26] R. H. McCoy, C. E. Meyer, and W. C. Rose, *ibid.*, p. 283.

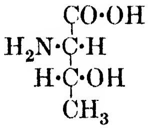
[27] *Ibid.*, p. 769.

[28] *Ber.*, 1934, **67**, 530.

centrate the active isomer by fractional crystallisation have not yet been successful. A more detailed study[29] of the amino-acid from natural sources involving its reduction to *d*-α-aminobutyric acid (which belongs to the *L* series) and its oxidation to *l*-lactic acid (which belongs to the *D* series) indicates that it corresponds in spatial structure to *d*(—)-threose (VII). It therefore has the configuration represented in (VIII). It is proposed to name it d(—)-*threonine*.

(VII).


$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{HO{\cdot}C{\cdot}H} \\ | \\ \mathrm{H{\cdot}C{\cdot}OH} \\ | \\ \mathrm{CH_2{\cdot}OH} \end{array}$$



$$\begin{array}{c} \mathrm{CO{\cdot}OH} \\ | \\ \mathrm{H_2N{\cdot}C{\cdot}H} \\ | \\ \mathrm{H{\cdot}C{\cdot}OH} \\ | \\ \mathrm{CH_3} \end{array}$$

(VIII).

F. Knoop, F. Ditt, W. Heckstedcn, J. Maier, W. Merz, and R. Hürle[30] have synthesised α-amino-β-hydroxy-γ-phenylbutyric acid and α-amino-β-hydroxy-δ-phenyl-*n*-valeric acid. Their study of these indicates that α-amino-β-hydroxy-acids are not degraded in the same way as simple amino-acids, but that they undergo β-oxidation and yield nitrogen-free acids. Presumably α-amino-β-keto-acids are formed, and these, they say, have a much greater redox potential than ascorbic acid.

Sulphur-containing Amino-acids.—Djenkolic acid[31] has been synthesised[32] by the action of methylene dichloride on the sodium derivative of cysteine in liquid ammonia, and its constitution confirmed as $CH_2[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_2$. From the same laboratory[33] comes a synthesis of glutathione with improved yields, the method employed differing from that of C. R. Harington and T. H. Mead[31] in that the SH group of the cysteine is protected by benzylation so that *S*-benzylcysteinylglycine is condensed with the α-monomethyl ester of *N*-carbobenzyloxyglutamic acid, and the final reduction is achieved by means of sodium in liquid ammonia.[34] A new synthesis of methionine has been published by E. M. Hill and W. Robson,[35] who treat ethyl γ-chloro-α-benzamidobutyrate (prepared from α-benzamido-γ-butyrolactone) with sodium methyl mercaptide, followed by alkaline hydrolysis, and hydrolyse the resulting benzoylmethionine with acid. It has been known for some time[36] that methionine is capable of replacing cystine in a cystine-deficient

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[29] C. E. Meyer, and W. C. Rose, *J. Biol. Chem.*, 1935, **115**, 721.

[30] *Z. physiol. Chem.*, 1936, **239**, 30.

[31] *Ann. Reports*, 1935, **32**, 418.

[32] V. du Vigneaud and W. I. Patterson, *J. Biol. Chem.*, 1936, **114**, 533.

[33] V. du Vigneaud and Miller, *ibid.*, 1936, **116**, 469.

[34] Cf. H. S. Loring and V. du Vigneaud, *ibid.*, 1935, **111**, 385.

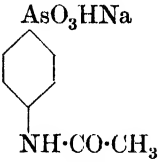
[35] *Biochem. J.*, 1936, **30**, 248.

[36] *Ann. Reports*, 1934, **31**, 340.

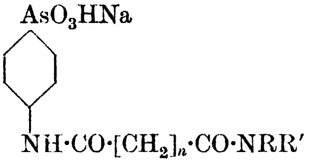
diet; now, however, it is suggested that the converse is not true, and that methionine is itself an "essential" amino-acid.[37]

Chemotherapy.

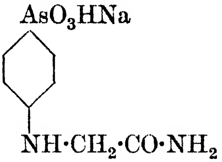
Trypanosomiasis and Syphilis.—G. T. Morgan and E. Walton [38] have studied compounds of the general formula (X)—for values of *n* ranging from 1 to 8 and in which R and R′ are either hydrogen, alkyl or aryl groups—in relation to arsacetin (IX) and tryparsamide (XI), which in all probability is the most widely used of the quinquevalent arsenical drugs. There does not appear to be any well-defined relationship between the chemical constitution and the therapeutic activity of these compounds. They exhibit varying degrees of curative action on experimental trypanosomiasis in mice, many of them having a therapeutic activity in trypanosome-infected mice which is at least equal to, if not greater than, that of tryparsamide. Branching of the carbon chain tends to diminish the activity and as the value of *n* in the straight chain approaches 8 there is considerable rise in toxicity. W. Yorke, F. Murgatroyd,[39] and their collaborators report very favourably on extensive trials of sodium succinanilomethylamide-*p*-arsonate (Neocryl) (X; $n = 2$; $R = H$, $R' = CH_3$), which is the most readily available of these derivatives, and they regard this compound as being more active than is tryparsamide on trypanosomiasis in laboratory animals. They record instances of its having effected definite clinical improvement in Nigerian sleeping sickness, in some cases with restoration of the cerebrospinal fluid to its normal state. They have found too that it differs from tryparsamide in its ability to exert a definite action in primary, secondary and tertiary syphilis, as distinct from neuro-syphilis.



(IX.)



(X.)



(XI.)

The latter group of workers [40] have long interested themselves in the important problem of arsenic-resistant strains of trypanosomes, their more recent investigations of the mechanism of the action of arsenicals on trypanosomes [40]—recently summarised by W. Yorke

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[37] W. C. Rose *et al.*, *J. Biol. Chem.*, 1936, **114**, lxxxv.

[38] *J.*, 1931, 615, 1743; 1932, 2764; 1933, 91, 1064; 1935, 290; 1936, 902.

[39] *Brit. Med. J.*, 1936, 1042.

[40] *Ann. Trop. Med. and Parasit.*, 1930, **24**, 449; 1931, **25**, 313, 351, 521; 1932, **26**, 215, 577; 1933, **27**, 157; *Brit. Med. J.*, 1933, 176.

and F. Murgatroyd[41]—being aided very materially by their fundamental discovery[42] of a satisfactory method whereby the pathogenic trypanosomes could be maintained *in vitro* for twenty-four hours at 37° in undiminished numbers and in a condition of unlowered vitality. Confirmation and extension of their findings are now accumulating from various sources. L. Launoy, M. Prieur, and A. Ancelot[43] have produced an arsenic-resistant strain of *T. annamense* in the guinea pig by repeated tryparsamide treatment and have found that, like the similarly produced arsenic-resistant *T. rhodesiense* of W. Yorke and his collaborators, it is thereby rendered resistant to the quinquevalent arsenicals and to a thioarsinite. C. H. Browning and R. Gulbransen[44] record experiments indicating that the immunity which develops after treatment with a curative drug depends on the particular strain of trypanosome and on the species of host. After studying the mode of action of a number of organic arsenicals on rats infected with *T. lewisi* and on rats infected with *T. equiperdum*, M. L. Kuhs, C. C. Pfeiffer, and A. L. Tatum[45] conclude that a specific relationship appears to exist between the type of arsenical and the type of trypanosome. The same authors[46] have made the interesting observation that infections of *T. lewisi* in rats which are easily cured by arsenophenylglycine provided that treatment is begun within 3—4 days of inoculation lose their arsenic susceptibility if there is further delay in commencing this treatment. T. Naito and S. Oka[47] have produced a strain of trypanosomes resistant to orsanine (3-acetamido-4-hydroxyphenylarsonic acid) and to the tervalent arsenicals neosalvarsan and neosilversalvarsan, and studied its sensitivity to other arsenical and non-arsenical drugs.

F. R. W. K. Allen[48] has treated nine cases of syphilis in India with a Merck preparation *Modenol*, a salicylate of arsenic and mercury, and eight of these cases have shown considerable improvement. A. B. Cannon and J. Robertson,[49] who set out to determine the relative values of bismuth and mercury preparations with arsphenamine in the treatment of early syphilis, have concluded that it is difficult to assay the relative values of bismuth and mercury, both of which are important in syphilis therapy. A

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[41] *Trans. Roy. Soc. Trop. Med. Hyg.*, 1935, **28**, 435; *W. Yorke. Riv. Malariol.*, 1935, **14**, Suppl.

[42] *Ann. Trop. Med. and Parasit.*, 1929, **23**, 501.

[43] *Bull. Soc. Path. exot.*, 1935, **25**, 857; 1936, **29**, 759.

[44] *J. Path. Bact.*, 1936, **43**, 478.

[45] *J. Pharm. Exp. Ther.*, 1936, **57**, 144.

[46] *Amer. J. Hyg.*, 1936, **23**, 10.

[47] *Z. Bakt.*, 1936, **137**, 401.

[48] *Indian Med. Gaz.*, 1936, 329.

[49] *J. Amer. Med. Assoc.*, 1936, **106**, 2133.

leading article in a recent issue of the *Lancet*[50] expresses the opinion that bismuth preparations are replacing mercurials in antisyphilitic treatment and makes special reference to the very favourable results of the tests by F. M. Thurmon[51] on some two hundred patients in his clinic over a period of eighteen months with a *fat-soluble* preparation, bismuth ethyl camphorate, either alone or in conjunction with arsphenamine. In these trials it compared favourably both as regards local pain or discomfort and more general toxic effects with the standard bismuth preparation—bismuth salicylate *suspended* in oil—which was in routine use on other patients in the clinic, and stress is laid on one particularly valuable feature of its activity, the efficiency of its mode of action in serological tests. W. M. Lauter and H. A. Braun[52] have prepared a series of bismuth trialkyl camphorates by allowing bismuth nitrate to react in aqueous glycerol with the appropriate sodium alkyl camphorate and have determined their toxicity on intramuscular injection into rats.

Malaria.—Preliminary reports[53] on the treatment of malaria with atebrin musonate (atebrin methyl sulphonate) have been promising. In recent months much evidence has been published which serves to substantiate the claims of atebrin and its musonate for wider clinical application. A. T. W. Simeons[54] has obtained very satisfactory results in the mass treatment of all persons in an endemic area with two injections of atebrin musonate at twenty-four-hour intervals. With atebrin, as with all synthetic preparations, claims on the grounds of therapeutic efficiency are considered together with cost of production. Thus J. A. Carman and R. P. Cormack[55] record the comparison of a number of cases of malaria in Kenya treated with atebrin musonate with an equal number of controls given quinine and plasmoquine. They consider that the results were as good as those of quinine treatment, with a probable lower relapse rate and without toxic symptoms, but they consider that the drug is uneconomical for use on natives. In contradistinction to this conclusion a large-scale trial of atebrin as a prophylactic in malarial regions of the Southern States, having shown that the drug is superior to quinine, producing complete destruction—not merely inhibition—of the parasites, has caused

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[50] 1936, 1163.

[51] *New Eng. J. Med.*, 1936, 315.

[52] *J. Amer. Pharm. Assoc.*, 1936, **25**, 394; cf. M. Picon, *Bull. Soc. chim.*, 1936, **3**, 176.

[53] *Ann. Reports*, 1935, **32**, 422; S. Somasundram, *Trans. Roy. Soc. Trop. Med. Hyg.*, 1935, **29**, 103; E. C. Vardy, *Malayan Med. J.*, 1935, **10**, 67.

[54] *Indian Med. Gaz.*, 1936, **71**, 132.

[55] *Trans. Roy. Soc. Trop. Med. Hyg.*, 1936, **29**, 381.

W. W. Bispham [56] to consider such treatment not only superior to quinine but actually cheaper in spite of the greater cost of the drug, for the simple reason that a smaller quantity suffices to effect a cure.

For all comparative work of this nature it is well to note the observation of F. Mietszch, H. Mauss, and G. Hecht [57] that aqueous solutions of atebrin decompose slowly on keeping with the formation of an acridone and falling off of toxicity, and the conclusion which S. F. Seelig and W. Singh [58] have drawn from a comparison of three methods of atebrin musonate treatment with or without adrenaline as to the most satisfactory method of administering the drug. They obtained the best and quickest results by giving adrenaline, followed by an intramuscular dose of atebrin musonate, and allowing twenty-four hours to elapse before commencing regular doses of atebrin tablets.

C. Ragiot and P. Moreau [59] have used quinacrine [60] with success in cases of hematuria due to quinine. O. J. Magidson and his collaborators [61] have continued to study the therapeutic activity with acridine derivatives closely allied to atebrin in relation to variations in chemical structure. From observations of malaria in children R. Sherman [62] considers that acriquine (6-chloro-9-diethylaminobutylamino-2-methoxyacridine) has a high therapeutic value. B. N. Rubenstein [63, 64] has found this same drug very successful for the treatment of induced malaria in paralytics and regards it as having a prophylactic action on experimental malaria in man.

In the study of monkey malaria anomalies in the behaviour of quinine and the various synthetic antimalarials have been noticed from time to time. Working with *Pl. Knowlesi* infections in apes, E. G. Nauck and B. Malamos [65] have furnished evidence in favour of the conception that atebrin and quinine are alike in one respect, that they exert a direct action on the malarial parasites, but that they differ in their mode of action in that the morphological changes which the parasites undergo are quite different for the two drugs and different from the changes in the controls.

[56] *Amer. J. Trop. Med.*, 1936, **16**, 547; cf. H. Flack, D. C. Majumder, and K. Goldsmith, *Indian J. Med. Res.*, 1936, **71**, 373.

[57] *Indian Med. Gaz.*, 1936, **71**, 521.

[58] *Records Mal. Survey Ind.*, 1936, **6**, 171.

[59] *Bull. Soc. Path. exot.*, 1936, **29**, 496.

[60] Identical in chemical constitution with atebrin.

[61] *Ber.*, 1936, **69**, 396, 537.

[62] *Med. Parasit. and Parasit. Dis.*, 1935, **4**, 446.

[63] *Arch. Schiff. Trop. Hyg.*, 1936, **40**, 167.

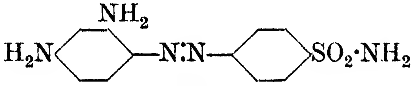
[64] *Med. Parasit. and Parasit. Dis.*, 1936, **5**, 256.

[65] *Klin. Woch.*, 1936, 888.

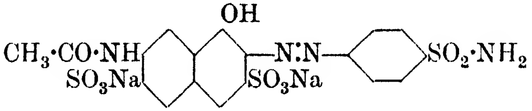
Antiseptics.—Noteworthy contributions have been made during the year under review to the problems of antisepsis. Investigations of the means of combating infection of the urinary tract discussed in an earlier report [66] still continue. G. H. Newns and R. Wilson [67] have found that mandelic acid in the form of its ammonium salt is an effective remedy for *B. coli* pyelitis in children. P. Ganguli [68] has employed the sodium salt. H. F. Helmholz and A. E. Osterberg [69] have studied both the urinary excretion of sodium mandelate and the bactericidal effect of this salt in various concentrations on a number of organisms, while in continuation of his pioneer work on the subject M. L. Rosenheim [70] has given an account of the treatment of almost one hundred cases of various types of urinary infection with ammonium mandelate.

The Prontosil group of antiseptics, derived from *p*-aminobenzenesulphonamide, of which *Prontosil* (XII) [71] and *Prontosil S* (XIII) [72]

(XII.)



(XIII.)



are at present the most efficacious, has come into prominence and is receiving considerable attention for the treatment of streptococcal and staphylococcal infections.[73] E. Fourneau, J. Tréfouël, F. Nitti, and D. Bovet [74] have observed that *p*-aminobenzenesulphonamide has an inhibitory effect on the growth of moulds which is not seen in prontosil, and F. Nitti and D. Bovet,[75] reviewing the present position of our knowledge of prontosil and its derivatives, note that guinea pigs can be sensitised to prontosil but

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[66] *Ann. Reports*, 1935, **32**, 425.

[67] *Lancet*, 1936, **230**, 1087.

[68] *Indian Med. Gaz.*, 1936, **71**, 517.

[69] *Proc. Mayo Clinic*, 1936, **11**, 373; *J. Amer. Med. Assoc.*, 1936, **107**, 1794; cf. L. P. Dolan, *ibid.*, p. 1800.

[70] *Lancet*, 1936, **230**, 1083.

[71] *Angew. Chem.*, 1935, 657.

[72] *Ibid.*, p. 661.

[73] K. Imhauser, *Klin. Woch.*, 1935, 282; L. Ley, *Münch. med. Woch.*, 1936, 1092; A. Roth, *Deut. med. Woch.*, 1935, 1734; C. Levaditi and A. Vaisman, *Compt. rend. Soc. biol.*, 1935, **119**, 946; 1936, **121**, 803; L. Colebrook and M. Kenny, *Lancet*, 1936, 1279, 1319; H. Hörlein, *Proc. Roy. Soc. Med.*, 1936, **29**, 313.

[74] *Compt. rend. Soc. biol.*, 1936, **122**, 652.

[75] *Revue d'Immun.*, 1936, **2**, 450, 461.

not to the parent substance. Prontosil and the more soluble prontosil S, administered intravenously or better orally, are gradually establishing themselves as successful means of combating erysipelas.[76] H. Floch [77] has administered prontosil orally with success in the treatment of elephantiasis. Numerous derivatives of *p*-aminobenzenesulphonamide [78] have been prepared, but there is as yet insufficient evidence on which to base a discussion of their therapeutic activity. The observation of R. Hilgermann [79] that alkali-metal salts of the bile acids, suitably protected by a colloid, can cure streptococcal infections opens up interesting possibilities.

C. P. S.
J. S.

Plant Biochemistry.

Metabolism and Biochemical Activity of Certain Bacteria.

Azotobacter.[1]—The production of free ammonia by these organisms has been the subject of much controversy. Earlier workers had disagreed not only on the question of whether or not the organism did actually produce free ammonia, but also as to whether this ammonia should be regarded as the first product of nitrogen fixation with subsequent elaboration into bacterial protein. S. Winogradsky,[2] working on silica-gel to avoid secondary reactions, confirmed his earlier adherence to the view that the nitrogen exchange of the organisms takes the course $N_2 \longrightarrow NH_3 \longrightarrow$ cellular protein, and that in very alkaline media a surplus of NH_3 appeared in the nutrient substrate. S. Kostytchev and O. Scheloumova,[3] following up previous investigations with *A. vinelandii*, added further support to Winogradsky's theories and also demonstrated that free ammonia was produced only in the presence of an adequate carbohydrate supply. Fixed nitrogen supplied to the organism was reduced to

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[76] L. Gmelin, *Münch. med. Woch.*, 1935, 221; W. Kramer, *ibid.*, 1936, 608; G. Scherber, *Wien. med. Woch.*, 1935, 284, 346, 376; E. Wehren, *Schweiz. med. Woch.*, 1936, **66**, 665; V. Anghelescu and collaborators, *Deut. med. Woch.*, 1936, 1639; K. Hartl, *ibid.*, 1936, 1641; J. Frankl, *Klin. Woch.*, 1936, **15**, 1562.

[77] *Bull. Soc. Path. exot.*, 1936, **29**, 165.

[78] P. Goissedet and collaborators, *Compt. rend. Soc. biol.*, 1936, **121**, 1082; E. Fourneau, J. Tréfouël, F. Nitti, and D. Bovet, *ibid.*, 1936, **122**, 258; G. A. H. Buttle, W. H. Gray, and D. Stephenson, *Lancet*, 1936, 1286; F. Nitti and D. Bovet, *Compt. rend.*, 1936, **202**, 1221.

[79] *Deut. med. Woch.*, 1936, 883.

[1] See *Ann. Reports*, 1933, 306.

[2] *Ann. Inst. Pasteur*, 1932, **48**, 269.

[3] *Z. physiol. Chem.*, 1931, **198**, 105.

ammonia and subsequently utilised in protein synthesis. He further showed that in the absence of a suitable carbon source cellular protein was itself deaminated with the formation of ammonia.

A. Isakova,[4] working with *A. vinelandii* and *A. chroococcum*, obtained similar results and demonstrated the production of ammonia in neutral or only very slightly alkaline media in which glucose, mannitol, or even salts of organic acids (sodium acetate, benzoate) formed the source of carbon. M. Roberg[5] and also D. M. Novogrudski[6] examined filtrates from *Azotobacter* cultures which were shown to contain nitrogen compounds utilisable by other micro-organisms (notably those utilising amino-acids or ammonia). Free ammonia, however, did not appear in the filtrates until the energy source had been exhausted by the bacteria. These results fall into line with an earlier suggestion of Kostytchev that ammonia found in culture media was largely derived from bacterial protein. Presumably any ammonia derived directly from nitrogen would be utilised by actively growing organisms as fast as it is formed. On the other hand A. N. Bach *et al.*[7] reported the production of ammonia from nitrogen by the expressed juice of *Azotobacter* cells, thus supporting the conception of the enzymic formation of ammonia as the first step in the nitrogen fixation process. In a series of detailed and carefully controlled experiments D. Burk and C. K. Horner,[8] continuing earlier investigations, showed that the extra-cellular production of ammonia by both *A. vinelandii* and *A. chroococcum* probably results almost entirely from the decomposition of cellular protein and not to any appreciable extent from free nitrogen. Under optimum aërobic conditions (p_H 7—8 and 30—40°) as much as 50% of the microbial nitrogen was liberated as ammonia. The presence of nitrogen was found to be quite unnecessary for ammonia production. The course of liberation of ammonia was closely paralleled by that of oxidation of cell constituents and was inhibited by reagents which normally check biological oxidations as well as by the presence of even small amounts of oxidisable organic matter. It is suggested that ammonia may not even be a necessary step in the synthesis of bacterial protein from nitrogen and that amides may be concerned here. In this connexion G. Endres[9] indicates the production of oximes in culture media of *Azotobacter* and suggests hydroxylamine as an intermediate stage in the fixation process. Burk

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[4] *Bull. Acad. Sci. U.R.S.S.*, 1933, **9**, 1493.

[5] *Jahrb. wiss. Bot.*, 1935, **82**, 1, 65.

[6] *Microbiol. U.S.S.R.*, 1933, **2**, 237.

[7] A. N. Bach, Z. V. Yermolieva, and M. P. Stepanion, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **1**, 22.

[8] *Soil Sci.*, 1936, **41**, 81.

[9] *Naturwiss.*, 1934, **22**, 662; *Annalen*, 1935, **518**, 109.

and Horner propound the following scheme of nitrogen exchange as being most in accord with experimental data :

$$N_2 + \text{organic matter} \xrightarrow[\text{growth}]{\text{enzymes}} \begin{array}{c}\text{stable cellular}\\ \text{compounds of}\\ \text{reduced N}\end{array} \underset{\text{growth}}{\overset{\text{deamination}}{\rightleftarrows}} NH_3.$$

From this point of view extracellular ammonia is liberated only under conditions in which growth is insufficiently rapid to permit the complete utilisation of the ammonia produced by the oxidative decomposition of the cellular constituents. The authors, however, point out that the data cannot be interpreted as definitely ruling out the possibility that some ammonia may be formed in the fixation process.

An examination of the cellular proteins of *Azotobacter* by R. A. Greene [10] indicates that these consist largely of globulins, glutelins, and albumins. The amino-acid distribution (Van Slyke) showed differences among the species, but in general arginine and lysine predominated and smaller proportions of tyrosine, tryptophan, cystine, and histidine together with approximately 40% of the non-basic fraction were found. The presence of glutathione was also indicated.

Another aspect of the activity of *Azotobacter* is presented by N. R. Dhar and colleagues,[11] who have shown that the fixation of nitrogen by these bacteria in tropical soils is optimum at 35°, as compared with 28° in temperate soils, and in both cases is negligible at 10°. It would seem, therefore, that the value of *Azotobacter* in maintaining the nitrogen supply in soil has been somewhat over-estimated. The addition of molasses to soil for the purpose of increasing fixation resulted in a rapid increase in the number of organisms, but the amount of nitrogen fixed did not increase proportionally. Rapid fixation is associated with more or less stationary numbers of *Azotobacter*. The improved nitrogen-status of molasses-treated soils, formerly attributed to increased bacterial fixation, is represented as being partly due, at least in tropical soils, to photochemical effects.

Among investigations of the influence of different carbon sources on the activity of *Azotobacter* may be cited that of S. Winogradsky,[12] in which it is shown that in addition to sugars, certain alcohols and simpler fatty acids (2—4 C) may be utilised. T. R. Bhaskaran and V. Subrahmanian,[13] working with mixed soil organisms in glucose

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[10] *Soil Sci.*, 1935, **39**, 327.

[11] N. R. Dhar and S. P. Tandon, *Proc. Nat. Acad. Sci. India*, 1936, **6**, 35; N. R. Dhar and E. V. Seshacharyulu, *ibid.*, p. 99; N. R. Dhar and S. K. Mukerji, *J. Indian Chem. Soc.*, 1936, **13**, 155.

[12] *Compt. rend.*, 1936, **203**, 10.

[13] *Current Sci.*, 1935, **4**, 234.

media, noted an initial period of activity, in which carbon dioxide and organic acids were formed from glucose, but the amount of nitrogen fixed was much less than that to be expected. Moreover much of this nitrogen was in a soluble form. Subsequently the organic acids were decomposed and apparently normal fixation proceeded. In a later paper [14] fixation of nitrogen by the mixed flora was shown to be facilitated by addition of organic acids obtained in the anaërobic decomposition of sugar. Utilising pure cultures of *A. chroococcum,* Bhaskaran [15] found no relationship between the presence of these sugar-decomposition products and the fixation of nitrogen, the course of which differed from that occurring with mixed soil cultures. It appears possible, however, that the acids contributed largely to the production of cellular constituents or perhaps served as energy sources. In young cultures the accumulation of carbon in the slime and bacterial cells was much more rapid than that of nitrogen. Later the ratio narrowed somewhat., G. Guittonneau and R. Chevalier [16] record that pure cultures of *Azotobacter* can utilise sodium salicylate and continue the fixation process.

Carbon Metabolism of, and Nitrogen Fixation by, Rhizobia.

The close relationship between the carbon metabolism and nitrogen exchange of these organisms referred to in a previous Report [17] continues to receive considerable attention at the hands of various research workers. Interesting data relating to the effect of nutritional factors on the respiratory quotient of cultures have now been obtained. Thus O. R. Neal and R. H. Walker [18] have examined the oxygen consumption of *R. meliloti* on glucose media, and have shown that the carbon dioxide produced corresponds to approximately one-third of the carbon in glucose, the amount being somewhat greater when ammonia than when nitrate forms the nitrogen source. The p_H optimum for growth of *R. meliloti* and *R. japonicum* appears to be less than that for respiration.[19] In a further publication O. R. Neal and R. H. Walker [20] record that the oxygen consumption of *R. meliloti* was substantially the same on glucose, mannitol, and sucrose media, but was very much greater on arabinose–nitrate media. Galactose was more effectively utilised than was glucose on both ammonia and nitrate media, whereas maltose, lactose, inositol,

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[14] *Proc. Indian Acad. Sci.*, 1936, **4**, *B*, 163.

[15] *Ibid.*, p. 67.

[16] *Compt. rend.*, 1936, **203**, 211.

[17] *Ann. Reports*, 1934, 347.

[18] *Proc. Iowa Acad. Sci.*, 1934, **41**, 167.

[19] D. W. Thorne and R. H. Walker, *J. Bact.*, 1935, **30**, 33.

[20] *Ibid.*, p. 173.

dulcitol, and sorbitol with both forms of nitrogen, and raffinose and erythritol in ammonia media, proved inferior energy sources. For this species ammoniacal nitrogen was in general more readily utilised than was nitrate. The reverse was true of *R. japonicum*, which also exhibited characteristic differences in its ability to utilise carbohydrates. Arabinose proved the best energy source, followed by glucose, galactose, and xylose, which were equally effective. Maltose, lactose, sucrose, mannitol, and erythritol were of little or no value in this respect. Subsequently Thorne, Neal, and Walker [21] determined changes in respiratory quotient with time for five species of *Rhizobia*, using different sources of nitrogen, and found characteristic species-differences in this case also. Comparing 24-hour cultures, the mean quotients for four nitrogen sources for *R. japonicum* and *R. leguminosarum* were definitely lower for *R. meliloti*, *R. trifolii*, and *R. phaseoli* in glucose media. In the absence of the sugar these differences disappeared. The mean quotients of the five species were similar on nitrate and on ammonia media with glucose, but were lower when yeast or asparagin was used to supply nitrogen. In the absence of glucose respiration in nitrate and ammonia media was largely endogenous and the quotient approached the theoretical value for protein, *viz.*, 0·8. Asparagin and yeast provided some carbon supplies and the quotients were lower in these cases, especially with yeast.

The much-discussed dependence of the nodulation of leguminous plants on the carbon : nitrogen balance of the plants themselves has been further examined by P. W. Wilson,[22] who traces characteristic effects of differences in C : N balance on the size and distribution of nodules, the amount and rate of nitrogen fixation, and the influence thereon of external conditions. On the basis of these effects a system of classification of plants in respect of their carbohydrate : nitrogen ratio is developed. An interesting review of the significance of the carbohydrate supply of the plant in the symbiotic relationship is given by F. E. Allison [23] who emphasises that, provided soil conditions are suitable, the activity of organisms within nodules is primarily controlled by the availability of carbohydrates, and that it is only when these become inadequate that the bacteria may make a direct attack on plant tissue. C. E. Georgi,[24] in examining the well-known effect of a supply of fixed nitrogen in reducing nodulation, showed that this condition is reflected in a temporary increase in the amount of carbohydrates and a decrease in that of nitrogenous

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[21] *Arch. Mikrobiol.*, 1936, **7**, 477.

[22] *Wisconsin Agric. Exp. Sta. Res. Bull.*, 1935, No. 129, 40 pp.

[23] *Soil Sci.*, 1935, **39**, 123.

[24] *J. Agric. Res.*, 1935, **51**, 597.

matter in the sap of red clover. The inhibitory action is diminished by further increasing the carbohydrate supply, *e.g.*, by increasing the supply of carbon dioxide to the leaves. Similar conclusions are reached by E. W. Hopkins [25] in the case of soya-bean organisms, the carbohydrate : nitrogen balance in this case being altered by varying the period of exposure and light, by partial shading, and by alteration of the nitrate supply of the plants. Whatever combination of external factors was adopted, the general conclusion is drawn that accumulation of soluble nitrogen in the plants restricted and that of carbohydrates favoured nodule formation. F. S. Orcutt and P. W. Wilson,[26] also working with soya bean to which varying supplies of nitrate were given, record similar results. Stress is laid, however, on the indirect effect of nitrates on nodulation, the carbohydrate level in the plant sap varying with the nitrate concentration in a manner similar to the intensity of nodulation. It is inferred that nodule formation is directly related to the carbohydrate supply and is affected by other conditions only to the extent to which these conditions influence the carbohydrate concentration in the plant. There is evidence that a definite rate of nitrate supply to the plant can be associated with the cessation of nitrogen fixation by the bacteria. Below the limiting value, the nitrate concentration increases or decreases nodulation according to whether photosynthesis or nitrogen supply becomes the limiting factor in protein formation, *i.e.*, whether there is a surplus of carbohydrate in the sap or a surplus of nitrogen, which is necessarily accompanied by a very low level of carbohydrate. H. G. Thornton and H. Nicol [27] support this view by showing that in sand-cultured lucerne the yield and nitrogen content of lucerne were not affected by varying (within limits) the amount of nitrate supplied. Presumably the limiting factor here was the carbohydrate produced by photosynthesis, and the nitrogen supply was derived from nitrate or from nodule organisms to meet requirements. Above certain concentrations of nitrate in the nutrient the number and size of nodules diminished. In other concentrations nitrates actually prevented the infection of growing roots by nodule organisms. This was to some extent counteracted by addition of glucose to the media.[28] In the latter paper Thornton recorded a stimulation of growth and an increase in the number of root hairs due to secretions from the nodule bacteria.

In many instances stimulation either of nodulation or of growth or nitrogen fixation by free cultures of nodule organisms has been observed following the addition of various substances. Thus S.

[25] *Soil Sci.*, 1935, **39**, 297.

[26] *Ibid.*, p. 289.

[27] *J. Agric. Sci.*, 1936, **26**, 173.

[28] H. G. Thornton, *Proc. Roy. Soc.*, 1936, *B*, **119**, 474.

Winogradsky [29] found the addition of simple nitrogen compounds, *e.g.*, ammonia, amines, amides, to otherwise nitrogen-free cultures improved the development and sugar consumption but caused no marked increase in the amount of nitrogen fixed. Addition of more substances such as extracts of yeast or of plant organs further increased development and initiated a normal rate of fixation of nitrogen. Similar results were obtained by A. Itano and A. Matsuura,[30] the activity of extracts being in the order seedlings > germinated > ungerminated seed, and among corresponding extracts of different species in the order, nodule-bearing legumes > non-legumes > non-nodule-bearing legumes. In a later paper [31] the same authors found the actual principle from bean nodules to pass into the cathode chamber on electrodialysis. In this respect it differed from yeast extract, in which the accessory substance showed no tendency to migrate. No relation was apparent between the activity of accessory substances and their nitrogen contents. Their action was that of a true growth-promoting substance rather than that of a nutrient. F. E. Allison and S. R. Hoover [32] attribute the increased growth of *Rhizobia* by natural, but not by synthetic, humic acid to the presence of co-enzyme *R*. This is the reverse of the view previously expressed by D. W. Thorne and R. H. Walker,[33] who ascribed the stimulatory effects of plant and yeast extracts to nutrient matter present and discredited the intervention of any co-enzyme in the activity of the organisms. A somewhat different view of this question was presented by C. A. Ludwig and F. E. Allison,[34] who observed increased nodulation of soya bean and lucerne when grown in sand cultures in the presence of other plants, *e.g.*, wheat or maize. Additions of sugar or small amounts of nitrogen compounds sometimes produced similar effects under these conditions, but extracts of the sand in which the plants had been growing were inactive. The excretion of stimulatory agents by the plant roots seems therefore excluded from consideration. The authors suggest that the presence of other plant roots induces in the rhizosphere conditions conducive to the development of the bacteria, possibly including the formation of a bacterial growth-promoting substance. Thorne, Neal, and Walker (*loc. cit.*) support the view that yeast extracts exert a stimulatory action on the growth and respiration of *Rhizobia*, which can be differentiated from that attributable to the carbonaceous and nitrogenous nutrients which they contain. The action of yeast is, how-

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[29] *Ann. Inst. Pasteur*, 1936, **56**, 221.

[30] *Ber. Ōhara Inst. landw. Forsch.*, 1936, **7**, 185.

[31] *J. Agric. Chem. Soc. Japan*, 1936, **12**, 457.

[32] *Soil Sci.*, 1936, **41**, 333.

[33] *Proc. Iowa Acad. Sci.*, 1934, **41**, 63.

[34] *J. Amer. Soc. Agronomy*, 1935, **27**, 895.

ever, ascribed to its ability to act as an effective hydrogen-donator to the organisms. This is in agreement with the observation of W. P. Allyn and I. L. Baldwin [35] that yeast, unlike potassium nitrate, when used as a nitrogen source for *Rhizobia* cultures, tends to maintain in the media an oxidation–reduction potential which is very favourable to the growth of the organisms. In a recent paper [36] Thorne and Walker record that reducing agents, *e.g.*, cysteine and thioglycollic acid, increased the growth and oxygen consumption of *Rhizobia*.

The nitrogen exchange of nodule organisms, especially in relation to the mechanism of the fixation process, and to the observed excretion of nitrogenous substances, has formed the subject of many investigations. According to A. I. Virtanen and M. Tornianen [37] the nodular proteins yield tryptophan, arginine, tyrosine, aspartic acid, and some diamino-acids. In culture media, following the growth of the inoculated legumes there are present aspartic acid, lysine, and smaller amounts of simpler compounds, *e.g.*, nitrite, nitrate, hydroxylamine or ammonia. Excretion of these compounds is dependent on appropriate supplies of air to the roots,[38, 39] and ceases when these are immersed in stagnant liquid media. The vitality of the organisms is not destroyed, however, since on re-aëration nitrogen fixation and excretion of fixed nitrogen continue. Virtanen concludes that the aspartic acid and probably the lysine excreted are not derived from nodular protein (the proteolytic activity of the organisms is apparently small [40]), but represent primary products of nitrogen fixation.[41, 42] It is suggested that aspartic acid may be formed from hydroxylamine and oxalacetic acid.[43] S. Winogradsky (*loc. cit.*) observed the elimination of ammonia from cultures to occur only during fixation of nitrogen.

G. Bond,[44] in an examination of the nitrogen exchange in soya bean, established that a very considerable proportion of the total nitrogen fixed by nodule organism (in some cases probably 80—90%) diffuses into the cytoplasm of the host plant and is translocated into the plant system. In a discussion of the fixation process the author considers this to resemble a type of respiratory activity rather than a stage in the synthesis of bacterial protein.

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[35] *J. Bact.*, 1932, **23**, 369.

[36] *Soil Sci.*, 1936, **42**, 231.

[37] *Suomen Kem.*, 1936, **9**, *B*, 13.

[38] A. I. Virtanen, *J. Agric. Sci.*, 1935, **25**, 278, 290.

[39] A. I. Virtanen and S. von Hausen, *ibid.*, 1936, **26**, 281.

[40] A. I. Virtanen and T. Laine, *Biochem. J.*, 1936, **30**, 377.

[41] *Idem*, *Suomen Kem.*, 1936, **9**, *B*, 12.

[42] A. I. Virtanen and M. Tornianen, *loc. cit.*, ref. (37).

[43] A. I. Virtanen and T. Laine, *Suomen Kem.*, 1936, **9**, *B*, 5.

[44] *Ann. Bot.*, 1936, **50**, 559.

Photosynthesis in Plants.

Influence of External Factors.—The complex problem of the effects of the quality and intensity of light, of the carbon dioxide concentration of the surrounding atmosphere, and of temperature on the rate of carbon assimilation of plants forms the subject of a great number of publications of the last few years. Much of this work follows along lines which are not altogether new in general principle but either develop an improved technique, expand the detail of experimental data, or, in the light of advancing knowledge, lead to new interpretations of already accepted facts. The application of the theory of limiting factors either as put forward by Blackman as a development of the " law of minimum," or with the modification (introduced by Harder) of the idea of relative minimum, served for a number of years as a working basis for much experimental work. More recent research tends to explore the limits of applicability of these theories. No attempt can be made in the space of this Report to give a comprehensive review of this field of enquiry, but some indication of the general trend of recent work seems desirable, especially in view of its ultimate bearing on the more purely chemical consideration of the mechanism of the photosynthetic process.

W. H. Hoover, E. S. Johnston, and F. S. Brackett [45] record data agreeing within limits with Blackman's law, and show that in wheat plants carbon assimilation exhibits a straight-line relationship with carbon dioxide concentration in an excess of light, and with light intensity in the presence of an excess of carbon dioxide. They indicate, however, a range of conditions between zones in which each limiting factor becomes dominant and conclude that this intermediate range is wider for higher plants than for algæ. B. N. Singh and K. N. Lal,[46] using wheat, linseed, and sugar cane plants, compare the results of much experimental work with the theories of Blackman and of Harder. The form of carbon dioxide concentration–assimilation curves obtained shows no sharp change of direction at a critical concentration such as would be anticipated if assimilation were controlled entirely by the level of supply of the factor in minimum (Blackman). The gradual and regular change of direction is more in accord with the view that factors other than that in minimum influence to a definite though relatively smaller extent the rate of carbon assimilation (Harder). The principal observations emerging are that under conditions of low carbon dioxide concentration and low light intensity the rate of assimilation is controlled by carbon dioxide. With high light intensity, however, irrespective

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[45] *Smithsonian Misc. Coll.*, 1933, **87**, No. 16.

[46] *Plant Physiol.*, 1935, **10**, 245; *Proc. Indian Acad. Sci.*, 1935, **1**, *B*, 909, 754.

of the level of carbon dioxide present, light controls assimilation. The influence of temperature on assimilation rates is also examined[47] and relationships are found to assume the same general nature. The temperature range over which assimilation takes place in radish leaves is recorded as 12·6—47·4°, with maximum values at 30°. It is concluded that under no conditions is assimilation determined by any one factor alone, but that, on the other hand, the theory of " relative minimum " is only of limited application. It is held that without consideration of the internal cellular mechanism of photosynthesis, no relationship between environmental factors can be applied as a general principle under all conditions.

The extent to which light of different wave-lengths can be utilised by plants varies somewhat with the species examined. Differences in the colour and thickness of leaves are partly concerned here (see further, under nutritional factors). G. R. Burns[48] shows that white pine and spruce utilise all the visible spectrum except the violet and part of the blue. Other plants, however, utilise the blue-violet range, and with this as sole illumination, assimilation is proportional to its intensity.[49] In general, however, rates of photosynthesis are highest in the red-orange region and decrease steadily toward the violet.[50, 51] As is to be expected, the percentage utilisation of light by different plants shows considerable variation. An instance of this is shown by recent work of Gabrielsen (*loc. cit.*), the alga *Chlorella* exhibiting a notably greater efficiency in this respect than mustard. The influence of the quality, as distinct from intensity, of light on the assimilation process has obvious practical bearings on greenhouse practice, and is frequently of prime importance in research work under conditions in which light of constant intensity must be obtained from artificial sources. In this connexion R. H. Dastur and K. M. Samant[52] have examined the relative rates of carbohydrate formation in leaves exposed to different sources of light. Their investigations suggest that in addition to the actual photosynthetic process the subsequent elaboration of carbohydrates may also be affected. Thus the amount of starch produced in artificial light was approximately 30% of that produced in daylight, whereas sucrose production was similar with both light sources. In diffused daylight the total carbohydrate production was double that obtained in artificial light. In plants producing no starch, *e.g.*,

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[47] B. N. Singh and K. Kumar, *Proc. Indian Acad. Sci.*, 1935, **1**, *B*, 736.

[48] *Plant Physiol.*, 1933, **8**, 247; 1934, **9**, 645.

[49] R. H. Dastur and R. J. Mehta, *Ann. Bot.*, 1935, **49**, 809.

[50] *Loc. cit.*

[51] E. K. Gabrielsen, *Planta*, 1935, **23**, 474.

[52] *Ann. Bot.*, 1933, **47**, 295.

Allium cepa, sugar production in diffused daylight was approximately three times that in artificial light. In these varied effects of different light sources, quality, rather than intensity, appears to be the dominant factor. On somewhat similar lines J. M. Arthur and W. D. Stewart [53] compared the efficiency of various artificial light sources on the basis of dry matter production in buckwheat plants. It is noted that the order of efficiency thus obtained differs from that shown by calculations on a basis of equal energy radiated within the visible spectrum. The efficiency of dry matter production in the plants did not appear to depend upon any relationship between the emission bands of the lamps and the absorption bands of chlorophyll pigments. Gaseous-discharge lamps (sodium, mercury, neon) by comparison with ordinary filament bulbs produced greener leaves and plants having lower stem : leaf ratios.

The ill-effect of ultra-violet light on the photosynthetic process under certain conditions is examined by W. Arnold [54] in the case of *Chlorella pyrenoidosa*, and is ascribed to its action in rendering inactive an unidentified unit in the mechanism of photosynthesis. Neither the chlorophyll nor the respiratory process is affected. O. Jírovec,[55] as a result of experiments with green and colourless strains of *Euglena gracilis*, concludes that chlorophyll normally affords partial protection against ultra-violet rays.

Plane-polarised light appears to cause no abnormality in the carbohydrate content of leaves.[56]

The influence of external factors on the relative ratio of carbon assimilation and of respiration becomes a matter of considerable importance in the investigation of photosynthesis. Not only do the two processes take place simultaneously with the same end-products, but also the " compensation point " in a closed system, *i.e.*, the condition in which respired carbon dioxide is quantitatively utilised in photosynthesis, is often regarded as an index value in studies of the influence of light or temperature on carbon assimilation. F. van der Paauw [57] showed that temperature produced parallel effects on respiration and assimilation in the green alga *Stichococcus bacillaris* and also, at temperatures less than 22°, in *Oocystis*. At higher temperatures in the latter and at lower temperatures in *Chlamydomonas* respiration responded more than assimilation to changes of temperature. With many other plants there was very close parallelism between rates of assimilation and respiration over the range

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[53] *Contr. Boyce Thompson Inst.*, 1935, **7**, 119.

[54] *J. Gen. Physiol.*, 1933, **17**, 135.

[55] *Protoplasma*, 1934, **21**, 577.

[56] R. H. Dastur and R. D. Asana, *Ann. Bot.*, 1932, **46**, 879.

[57] *Planta*, 1934, **22**, 396.

10—30°. Moreover mild stimulation or retardation of both processes could be effected by appropriate treatment with potassium cyanide.[58] Somewhat similar results were obtained by E. S. Miller and G. O. Burr,[59] who determined the compensation point for a number of plants, using a special apparatus in which the upper portions of the plants were subjected to light of high intensity but the roots were kept relatively cool. Plants of various species quickly reduced the concentration of carbon dioxide in the circulating air to a level of 0·01% (vol.), which was maintained for periods of 24 hours. This value did not change with temperature in the range 5—35°. Since the respiration rate is known to increase by as much as 15 times over this range, and under the conditions of the experiment light was always in excess, it is concluded that the limiting factor in assimilation is not the primary process of light absorption but the intermediate reaction which is controlled by the carbon dioxide concentration; also that the temperature coefficient of this reaction is identical with that of respiration. The utilisation of the increased products of respiration without increase in carbon dioxide concentration is ascribed to the assimilation of an intermediate product of respiration before any carbon dioxide is liberated from it, a possibility which was suggested previously by Warburg. At 35—37° the above relations appear to break down rapidly and the gas exchange of different species shows wide variations.

The dependence of the rate of photosynthesis on the water content of the leaf is examined by a number of workers.[60, 61, 62] In general a more or less direct relationship is established up to a critical water content, beyond which assimilation tends to decline. Dastur (*loc. cit.*) determines the " assimilation number " of various plants (*i.e.*, H_2O content/CO_2 assimilated) and finds this to increase with rising water content to an optimum value and subsequently to decrease. Comparison with Willstätter's " assimilation number " (*i.e.*, chlorophyll content—CO_2 assimilated) shows a much closer relationship of assimilation with the water than with the chlorophyll content.

The lack of proportionality between chlorophyll content of leaves and assimilation observed in many cases by Willstätter and by subsequent workers does not apparently obtain in the case of *Chlorella*, in which a direct ratio is established by W. E. Fleischer,[63] even when the chlorophyll content is artificially varied by controlling the supply

[58] F. van der Paauw, *Rec. Trav. bot. néerl.*, 1932, **29**, 497.

[59] *Plant Physiol.*, 1935, **10**, 93.

[60] R. Melville, *Ann. Rept. Exp. Sta. Cheshunt*, 1933, 87.

[61] B. N. Singh and K. N. Lal, *Ann. Bot.*, 1935, **49**, 291.

[62] R. H. Dastur and B. L. Desai, *ibid.*, 1933, **47**, 69.

[63] *J. Gen. Physiol.*, 1935, **18**, 573.

of iron. R. Emerson,[64] with somewhat different experimental conditions, had made similar observations, and further recorded that light conditions giving optimum assimilation rates in leaves rich in chlorophyll were also optimum for those poor in chlorophyll. Possibly this case resembles that of *Elodea densa*, examined by E. von Euler, B. Bergman, and H. Hellström,[65] in which the chlorophyll content per chloroplast and the number of chloroplasts per cell were substantially constant.

Mechanism of Photosynthesis.—The complexity of the effects of environmental conditions and of internal plant factors on carbon assimilation observed directly by plant physiologists has been paralleled by the more purely chemical investigations of the complexity of chlorophyll.

Recent years have brought a much more complete understanding of the chemistry of chlorophyll [66] and related compounds, but the means by which chlorophyll brings about the conversion of carbon dioxide into carbohydrate is still the subject of controversy. It is very generally accepted that formaldehyde represents an intermediate stage in the conversion and that the change $CO_2 + H_2O \longrightarrow CH_2O + O_2$ is effected (probably in the absence of light) with the aid of light energy previously absorbed by the chlorophyll. Theories of the mechanism of photosynthesis differ considerably in detail, but are centred round considerations of whether the fundamental energy exchange involves carbon dioxide, water, oxygen, or the chlorophyll itself. Warburg originally supposed that the chlorophyll (and carotene) in leaves was transformed into an isomeric substance during exposure to light and in the subsequent (dark) reaction the isomer, a reducing agent, caused the transformation of carbonic acid into formaldehyde and water. By contrast among the earlier theories, that of Thunberg supposed the absorbed light energy to act on the water associated with chlorophyll rather than on carbon dioxide, the chain of reactions being :

$$2H_2O + \text{chlorophyll} + \text{light} \longrightarrow H_2 + H_2O_2$$

$$CO_2 + H_2 + H_2O_2 \longrightarrow O_2 + H_4CO_2$$

(? methyleneglycol)

$$H_4CO_2 \longrightarrow CH_2O + H_2O$$

As will be shown, these and other early theories of assimilation have reappeared in recent years, modified or extended to bring them into accord with newly observed facts.

E. C. C. Baly,[67] after prolonged investigation of relevant catalytic

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[64] *J. Gen. Physiol.*, 1929, **12**, 609; *Proc. Nat. Acad. Sci.*, 1929, **15**, 281.

[65] *Ber. deut. bot. Ges.*, 1934, **52**, 458.

[66] *Ann. Reports*, 1935, 362.

[67] *Proc. Roy. Soc.*, 1935, *B*, **117**, 218.

actions, has now formulated the primary photosynthetic reaction as depending in the absorption of carbon dioxide by chlorophyll-*a*, the photosensitised complex changing to chlorophyll-*b* and formaldehyde. The cycle is completed by reduction in the dark (Blackman reaction) of chlorophyll-*b* to chlorophyll-*a*, the reducing agent suggested being carotene. Thus :

$$\underset{\textit{chlorophyll-}\mathrm{a}\text{-}\mathrm{CO_2}\textit{ complex.}}{C_{55}H_{72}O_5N_4Mg\text{-}CO_2,H_2O} \xrightarrow{\text{light}} \underset{\textit{chlorophyll-}\mathrm{b}.}{C_{55}H_{70}O_6N_4Mg,H_2O} + CH_2O$$

$$\underset{\textit{chlorophyll-}\mathrm{b}.}{C_{55}H_{70}O_6N_4Mg,H_2O} + \underset{\textit{carotene.}}{C_{40}H_{56}} \longrightarrow \underset{\textit{chlorophyll-}\mathrm{a}.}{C_{55}H_{72}O_5N_4Mg} + \underset{\textit{xanthophyll.}}{C_{40}H_{56}O_2}$$

The kinetics of these reactions are shown to be in accord with published experimental data relating to the carbon assimilation of *Chlorella.*

By mathematical consideration of the effects of temperature and light intensity on carbon assimilation G. E. Briggs [68] indicates a system involving the formation of a chlorophyll–CO_2 complex which in light undergoes molecular rearrangement to a peroxidised substance. This is decomposed through the agency of plant catalysts, yielding carbohydrate and oxygen, or, in part, decomposes an inhibitor (present in the cell) which inactivates the catalyst. The classic researches of Willstätter and Stoll had previously led to similar views. More recently there has appeared some divergence between the theories of Willstätter and of Stoll, the differences centring on the position of oxygen as a necessary agent in the first stages of the assimilatory process. A. Stoll [69] assumes that chlorophyll-*a* and -*b* contain a " supernumerary " double linking outside the conjugated system, which permits catalytic hydrogenation without significant change in the absorption spectrum.[70] The dihydro-derivative is easily dehydrogenated and serves as reducing agent for the chlorophyll–CO_2 complex, yielding formaldehyde. Rehydrogenation of the chlorophyll results from the fission of water closely associated with it,

$$H_2O \longrightarrow H + OH\ (\longrightarrow H_2O_2),$$

the hydrogen peroxide being subsequently decomposed by the catalase of the leaf. In a later publication [71] Stoll brings his scheme more closely into line with recent developments in the elucidation of the structure of chlorophyll. The catalytic hydrogenation of chlorophyll is now known to yield a dihydro-derivative by addition at the

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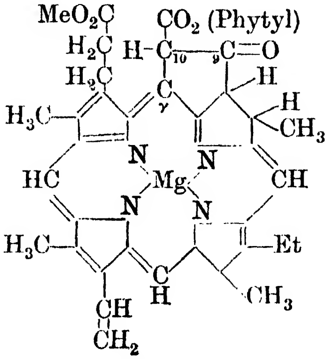
[68] *Proc. Roy. Soc.*, 1933, *B*, **113**, 1.

[69] *Naturwiss.*, 1932, **20**, 955.

[70] *Loc. cit.*; also R. Kuhn and A. Winterstein, *Ber. deut. bot. Ges.*, 1932, **65**, 1737.

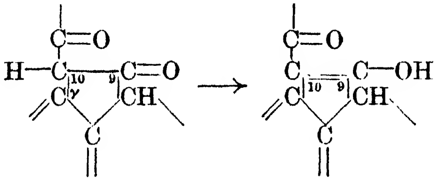
[71] *Naturwiss.*, 1936, **24**, 53.

double bond of the vinyl group, a position in which mobility or the easy interaction with carbon dioxide co-ordinatively attached to the central magnesium atom seems unlikely. Accepting Fischer's formula for chlorophyll (I), Stoll now associates photoactivity with the mobility of the hydrogen atom in position 10 (Fischer having now introduced the two "extra" hydrogen atoms into the structure).



(I.)

An enolisation taking the form

(II.)


(III.)

is indicated as related to the brown phase in the chlorophyll cycle. The hydrogen attached to the carbon C_{10} in (II) may be replaced by hydroxyl and in this substance the hydrogen on C_{10} becomes mobile in daylight (but not in darkness) provided atmospheric oxygen is excluded. Stoll, therefore, although reconstructing his earlier mechanism, still retains his primary conception that oxygen is not an immediately active agent in photosynthesis, which is more accurately represented as involving a photolysis of water as a result of the principal energy exchange.

On somewhat similar lines K. Shibata and E. Yakushiji [72] assume the co-ordination of four water molecules with the central magnesium atom of the chlorophyll. These become activated by the absorbed light in such a manner that the reaction,

$$H_2CO_3 + 4(H\ .\ .\ .\ OH) = 2H_2O + CH_2O + 4OH(= 2H_2O_2)$$

is facilitated. Here again oxygen is not immediately concerned and the associated water molecules are the vehicle of the energy exchange,

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[72] *Naturwiss.*, 1933, **21**, 267.

four quanta being involved. The Blackman (dark) reaction is represented by the decomposition of hydrogen peroxide by catalase, this being the sole source of oxygen in the system.

H. Gaffron [73] supports the conception that the assimilation process does not necessitate the intervention of an activated or metastable oxygen atom.

By contrast to the above Willstätter's later work [74] leads him to assume the necessity of at least a small amount of oxygen to initiate the activity of chlorophyll. He also differs from Stoll in supposing the photosynthetic cycle to involve the formation of dehydrogenated chlorophyll derivatives. The formation of actively reducing hydrogen atoms is represented schematically by an initial reaction of chlorophyll with oxygen, yielding monodehydrochlorophyll:

$$\text{chlorophyll} + O_2 \longrightarrow (O_2H) + \text{monodehydrochlorophyll}.$$

The wandering of a hydrogen atom into the Mg–CO_2 complex yields dehydrochlorophyll. Then follows,

$$\text{dehydrochlorophyll} + H_2O \longrightarrow OH + \text{monodehydrochlorophyll}$$

and again

$$\text{monodehydrochlorophyll} \longrightarrow \text{dehydrochlorophyll} + H,$$

the H going to the Mg–CO_2 complex. This cycle is completed four times, yielding the necessary four hydrogen atoms for the reduction of one molecule of carbon dioxide. The process is assumed to proceed in stepwise manner, each hydrogen atom reacting singly. Regeneration of chlorophyll in light is effected thus,

$$\text{dehydrochlorophyll} + H_2O \longrightarrow OH + \text{monodehydrochlorophyll}$$
$$\text{monodehydrochlorophyll} + H_2O \longrightarrow OH + \text{chlorophyll}.$$

The radicals O_2H and OH formed intermedially either take part in a further hydrogenation cycle or yield H_2O, O_2 and H_2O_2 according to the environmental conditions which regulate the intensity of the various stages of the reaction.

J. Franck [75] supports Willstätter's view of the necessity of oxygen for the process, but considers that photochemical reactions in solution are more likely to occur by means of reactions of activated molecules than through the formation of radicals [76] as indicated by Willstätter. With this in view and with the purpose of adjusting the cycle of changes to accord more satisfactorily with calculated energy relationships, Franck modifies Willstätter's system by assuming a somewhat different series of intermediates, and, adopting

[73] *Biochem. Z.*, 1935, **280**, 337; 1936, **287**, 130.

[74] R. Willstätter, *Naturwiss.*, 1933, **21**, 252.

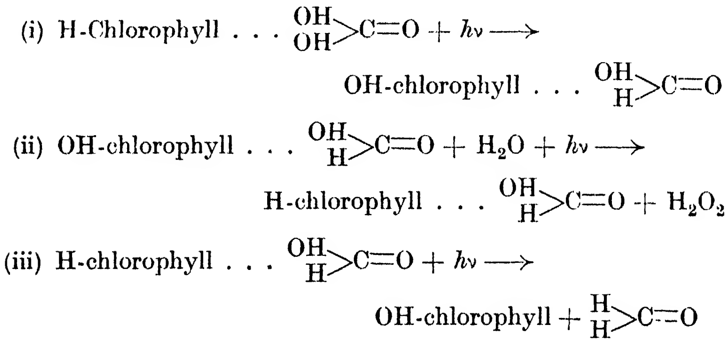
[75] *Naturwiss.*, 1935, **23**, 226.

[76] J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, 1934, **152**, No. 30.

Fischer's views, includes in the chlorophyll molecule the two loosely bound hydrogen atoms. To make the comparison with Willstätter's scheme more evident, he designates ordinary chlorophyll as HH-chlorophyll, monodehydrochlorophyll as H-chlorophyll, dehydrochlorophyll as "chlorophyll," and dehydrochlorophyll, to which a hydroxyl group is loosely attached, as OH-chlorophyll. The preliminary (light) reaction involves dissociation of one of the two loosely bound hydrogen atoms,

$$\text{HH-chlorophyll} + h\nu \longrightarrow \text{H-chlorophyll} + \text{H}$$

the hydrogen atom being taken up in a series of changes with water and oxygen (as in Willstätter's scheme) with the ultimate formation of hydrogen peroxide, and H-chlorophyll combining with carbonic acid. The actual assimilation process is represented as :



$$\text{(i) H-Chlorophyll} \ldots \begin{smallmatrix}OH\\OH\end{smallmatrix}\!>C{=}O + h\nu \longrightarrow \text{OH-chlorophyll} \ldots \begin{smallmatrix}OH\\H\end{smallmatrix}\!>C{=}O$$

$$\text{(ii) OH-chlorophyll} \ldots \begin{smallmatrix}OH\\H\end{smallmatrix}\!>C{=}O + H_2O + h\nu \longrightarrow \text{H-chlorophyll} \ldots \begin{smallmatrix}OH\\H\end{smallmatrix}\!>C{=}O + H_2O_2$$

$$\text{(iii) H-chlorophyll} \ldots \begin{smallmatrix}OH\\H\end{smallmatrix}\!>C{=}O + h\nu \longrightarrow \text{OH-chlorophyll} + \begin{smallmatrix}H\\H\end{smallmatrix}\!>C{=}O$$

$$\text{(iv) OH-chlorophyll} + H_2O + h\nu \longrightarrow \text{H-chlorophyll} + H_2O_2$$

By assuming differences in the energy of combination of hydrogen and of hydroxyl in themselves, and in relation to position in the co-ordinated magnesium complex or the chlorophyll residue, Franck brings the above cycle of reactions into line with the accepted energy balance of the complete assimilation process.

Evidence of a vital part played by oxygen in the photosynthetic process is put forward by H. Kautsky and colleagues and is based on phenomena of an entirely different character. Following an extensive study of photosensitised surface reactions, including those concerned in fluorescent conditions, Kautsky concluded that in many surface oxidations the presence of an activated or metastable oxygen atom is essential to effect the energy transfer. A green leaf which has been placed in the dark for a period and afterwards exposed to ultra-violet light exhibits a temporarily increased fluorescence, followed by a steady decline to a low level which is substantially constant in unchanged external conditions. The process, lasting at most a few minutes, may be repeated indefinitely by alternate exposure of the leaf to darkness and to light.

In examining these changes H. Kautsky, A. Hirsch, and F. Davidshofer [77] associate the fluorescence with changing intensities of different stages of the photosynthetic process. The photosensitised chlorophyll is able to transfer its energy only to a molecule of definite type. Of those present in the leaf system, only oxygen fulfils this requirement, and the presence of activated or metastable oxygen in the leaf plastids is assumed.[78] The transference of energy to oxygen lowers the intensity of fluorescence. The energised oxygen effects the building up of the chlorophyll–carbon dioxide–peroxide complex,[79] resulting ultimately in the production of carbohydrate and oxygen. The increase in the oxygen supply brought about in this way results in a still further decrease in fluorescent intensity. (declining portion of curve) until a balanced condition is reached between light absorption, fluorescence, and oxygen transfer, which is characteristic of the normal condition of assimilation. The rate of initial increase in fluorescence under these conditions is controlled by the intensity of irradiation, but is unaffected by temperature.[80] The second stage of the assimilation process (reactions involving the chlorophyll–CO_2 complex and the final production of carbohydrate) is definitely restricted by decreased temperature and also by treatment with hydrocyanic acid or toluene, and such restriction, by lowering the supply of photosynthetically derived oxygen, causes a prolongation or an increased intensity of the fluorescence.[81] An artificially increased concentration of carbon dioxide in the atmosphere (to 1%) has no influence on the course of fluorescence, but variations in the oxygen concentration cause corresponding changes in intensity. A critical point is apparently reached with 0·5% of oxygen, below which fluorescence does not increase with the intensity of irradiation.[82] In an atmosphere free from oxygen leaves fluoresce with high and constant intensity until liberation of oxygen causes a diminution to the normal equilibrium level.[83] In a later and more detailed examination of fluorescence curves, Kautsky [84] traces the course of activation of the chlorophyll–O_2 complex and finds it to be of a unimolecular type. In the light of this and previous observ-

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[77] *Ber.*, 1932, **65**, 1762.

[78] H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister, *Ber.*, 1933, **66**, 1588.

[79] H. Kautsky and A. Hirsch, *Naturwiss.*, 1931, **19**, 964.

[80] H. Kautsky and H. Spohn, *Biochem. Z.*, 1934, **274**, 435.

[81] H. Kautsky and A. Hirsch, *ibid.*, 1935, **277**, 250.

[82] H. Kautsky and W. Flesch, *ibid.*, 1936, **284**, 412.

[83] H. Kautsky and A. Hirsch, *ibid.*, 1935, **278**, 373.

[84] H. Kautsky and A. Marx, *Naturwiss.*, 1936, **24**, 317.

ations he considers that in the darkened leaf the equilibrium, chlorophyll + $O_2 \rightleftharpoons$ chlorophyll–O_2 complex, $[Ch]O_2$, in the plastids is normally balanced almost completely to the right. The complex is dissociable but non-fluorescent. On irradiation $[Ch]O_2$ undergoes rearrangement to form a new non-dissociable but fluorescent complex $[ChO_2]$, probably a peroxidised form. This unimolecular change corresponds with the initial increase in the fluorescence curve. J. Franck [85] doubts the physical soundness of Kautsky's views of the properties of a metastable oxygen molecule, and considers the fluorescent changes are more in agreement with the existence of mobile hydrogen atoms bound to the chlorophyll molecule. The rising part of Kautsky's fluorescence curves may well be represented by the change

$$\text{HH-chlorophyll} \longrightarrow \text{H-chlorophyll.}$$

H. Gaffron [86] also criticises Kautsky's interpretation of the experimental data, and advances evidence, based on the carbon assimilation of *Chlorella*, in support of his view that neither free nor loosely bound oxygen is necessary for the initiation of the assimilation process.

H. H. Strain [87] recently reports the isolation of two crystalline fluorescent substances from leaves, both of which actively absorb ultra-violet light, especially in the shorter wave-lengths. Both resist saponification, but gradually lose their characteristic properties on exposure to air. The fluorescent spectra indicate the absence of ester, carboxyl or hydroxyl groups. The fact that one or both of these substances occurred in leaves of all plants examined suggests that they may have an interesting bearing on Kautsky's observations.

From considerations of the photobleaching of fluorescent dyes in an oxygen-free atmosphere by the action of ferrous salts J. Weiss [88] suggests the reaction

$$Fe^{\cdot\cdot} + HOH + h\nu = Fe^{\cdot\cdot\cdot} + OH' + H$$

may explain the vital change taking place in the case of chlorophyll as with the photosensitised dyes, and recalls the observation of K. Noack [89] that chloroplasts in leaves contain appreciable proportions of ferrous iron.

An interesting discussion of the energy relationships in the various theories of the photosynthetic mechanism is given by H. Gaffron and K. Wohl.[90]

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[85] *Op. cit.*; also J. Franck and H. Levi, *Naturwiss.*, 1935, **23**, 229.

[86] *Biochem. Z.*, 1933, **264**, 270; *Naturwiss.*, 1935, **23**, 528.

[87] *Nature*, 1936, **137**, 946.

[88] *Ibid.*, 1935, **136**, 794.

[89] *Z. Bot.*, 1930, **23**, 957.

[90] *Naturwiss.*, 1936, **24**, 18, 103.

Condition of Chlorophyll in the Plant.

It has long been assumed that in the leaf chlorophyll exists in a colloidal condition. The fact that chlorophyll cannot be extracted from dried leaves by certain organic solvents until water has been added, has suggested that in the chloroplast chlorophyll occurs in some form of labile combination or elaborate physical state from which it is released or dissociated by means of water.

Moreover it has been shown [91, 92, 93] that in the assimilation process some 1500—2000 molecules of chlorophyll (Emerson and Arnold's " photosynthetic unit ") must be present to effect the transfer of the four light quanta (necessary for reduction) to one molecule of carbon dioxide. This contributes to the view that some differentiation between the chlorophyll molecules is likely in respect of their physical or chemical condition.

Recent observations, among which may be cited those of W. Mencke,[94] L. G. M. Baas-Becking and H. C. Koning,[95] and J. G. Wakkie,[96] lend further support to the conception that the physical condition of chlorophyll in leaves is a somewhat complex one. A colloidal state seems unlikely and the absorption and fluorescence spectra indicate that chlorophyll cannot be present in simple solution. Mencke suggests that two phases are present: one, a lipoid phase in which the chlorophyll is dissolved in the lipoid constituents of the plastid, and an aqueous phase in which the lipoid solution is dispersed. B. Hubert [97] indicates that if chlorophyll is in solution it must be in a medium of very high refractive index, and concludes that a condition of adsorption is probable.

Discussing Mencke's views, J. Weiss [98] points out that, if a lipoid solution of chlorophyll is dispersed in an aqueous phase in the chloroplast, a considerable portion of the absorbed light may be stored by molecules of chlorophyll in the interior of the lipoid phase as a form of electronic excitation energy, and may be passed from molecule to molecule by a " resonance " effect. Only those molecules at the lipoid–aqueous interface react with carbon dioxide, but in time the whole of the energy stored by the " internal " molecules may reach the " surface " molecules and bring about the formation of the chlorophyll–CO_2 complex. In weakly assimilating leaves, energy reaching the surface may not be entirely utilised and will appear as

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[91] R. Emerson and W. A. Arnold, *J. Gen. Physiol.*, 1932, **16**, 191.

[92] W. A. Arnold and H. I. Kohn, *ibid.*, 1934, **18**, 109.

[93] H. I. Kohn, *Nature*, 1936, **137**, 706.

[94] *Protoplasma*, 1934, **21**, 279.

[95] *Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 674.

[96] *Ibid.*, 1935, **38**, 1082.

[97] *Ibid.*, 1934, **37**, 694.

[98] *Nature*, 1936, **137**, 997.

fluorescence. This accords with Kautsky's observation that fluorescence in some cases bears an inverse relation to the rate of assimilation. The " photosynthetic unit " may also be regarded as directly related to the ratio of " surface " : " internal " molecules, in which case some 400—500 molecules of chlorophyll are present in the interior of the lipoid phase for each actively assimilating " surface " molecule.

The possibility of labile compounds of chlorophyll and protein is examined by R. S. Hilpert and K. Heidrich,[99] who show that a definite portion of " mobile " protein, different from the general protein of the leaf, can be associated with chlorophyll in all organs of the plant and in all stages.

A. Stoll[1] discuss a further development of the chlorophyll–protein complex theory. In the light of Willstätter's explanation of the activity of lactoflavin, *viz.*, the formation of a " Symplex," lactoflavin-phosphoric acid–colloid carrier, Stoll suggests the presence in the plastids of a symplex (" chloroplastin "), chlorophyll–colloid carrier [? protein]. The symplex may be assumed to dissociate in the presence of water containing dissolved electrolytes from the leaf. The insolubility of chlorophyll from dried leaves in certain organic solvents is thereby explained. The point of attachment of the colloid is possibly the double bond of the vinyl side chain. On this basis the actual absorption of light and its transformation into potential chemical energy is associated with the chlorophyll molecule and is independent of temperature. The subsequent production of formaldehyde (temperature sensitive) may be regarded as an enzymic reaction since the symplex has an enzyme-like structure. The chlorophyll–colloid (protein) combination may thus be regarded as a specific assimilating enzyme.

Chlorophyll Formation in Plants and Nutritional Factors affecting it.

Nitrogen.—In addition to the environmental influences already discussed, genetic,[2] nutritional[3] and physiological[4] factors are concerned in the production of chlorophyll in plants. Recent work has in many cases thrown further light on the manner in which these indirect and often less obvious factors affect the photosynthetic activity of plants.

An adequate supply of nitrogen to plants is obviously necessary

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[99] *Ber.*, 1934, **67**, 1077.

[1] *Naturwiss.*, 1936, **24**, 53.

[2] H. von Euler *et al.*, *Svensk Kem. Tidskr.*, 1934, **46**, 301; *Z. physiol. Chem.*, 1935, **233**, 81; **234**, 151.

[3] W. Mevius, *Jahrb. wiss. Bot.*, 1935, **81**, 327.

[4] B. N. Singh and K. N. Lal, *Ann. Bot.*, 1935, **49**, 291; W. E. Loomis and K. H. Burnett, *Proc. Iowa Acad. Sci.*, 1931, **38**, 150.

for the actual elaboration of the chlorophyll molecule. It is also generally recognised that conditions favouring rapid vegetative growth are in general those which favour chlorophyll production. A generous nitrogen supply is a prominent factor in this. It might therefore be anticipated that a deficient nitrogen supply could operate as a limiting factor in chlorophyll production on much the same lines as it does in gross dry-matter formation in the growing plant. A relationship of this kind is indicated by the work of R. K. Tamm and O. C. Magistad.[5] In pineapple leaves the chlorophyll content tended to increase uniformly with the amount of nitrogenous fertiliser applied, up to a limiting amount. Very large applications resulted in a decrease in chlorophyll production. F. M. Schertz,[6] examining chlorotic mottling in leaves, found this could be corrected by treatment with sodium nitrate. Moreover the customary correctives, iron and manganese, for chlorosis were ineffective if the nitrogen supply was inadequate. It was later shown that the level of nitrogen supply could be correlated directly with pigment formation in the chloroplast. J. D. Guthrie [7] also records that nitrogen deficiency had little influence on the chlorophyll content of plants in winter (when factors other than nitrogen limit growth), but during rapid spring growth chlorophyll production was restricted by a partial deficiency of nitrogen. The form in which nitrogen is supplied to the plant affects the nitrogen–chlorophyll as well as the nitrogen–growth relationship. G. B. Ulvin,[8] working with sugar-cane, found that nitrate-fed plants produced more chlorophyll than did those supplied with ammonium salts.

The observation by G. Gassner and G. Goeze [9] of a direct relationship between the protein and the chlorophyll content of cereal plants seems to add further confirmation of the significance of nitrogen nutrition in the formation of chlorophyll.

Potassium.—The close relation between potassium and the assimilatory process in plants is very generally recognised. It is usually considered that potassium acts in this respect by regulating enzyme activity rather than through any direct influence on the chlorophyll itself. Such an influence is, moreover, difficult to establish experimentally owing to the varied ways in which potassium influences the functional activities of the plant.

Lundegårdh [10] observed that at moderately high temperatures (20—30°) assimilation in potassium-deficient leaves was greater than

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[5] *Plant Physiol.*, 1935, **10**, 159.

[6] *Bot. Gaz.*, 1921, **71**, 81; *Plant Physiol.*, 1929, **4**, 269.

[7] *Amer. J. Bot.*, 1929, **16**, 716.

[8] *Plant Physiol.*, 1934, **9**, 59.

[9] *Ber. deut. bot. Ges.*, 1934, **52**, 321.

[10] "Die Nährstoffaufnahme der Pflanzen," 1932.

in those adequately supplied and that this difference was related to the higher chlorophyll content of the deficient leaves. In older leaves from which much of the normal potassium content had been eliminated, assimilation was restricted. Gassner and Goeze [11] associate "moderate" potassium deficiency with a maximum chlorophyll content in wheat leaves, and simultaneously with maximum assimilation and respiration. A more severe deficiency of potassium has a definite inhibitory effect on all factors. It seems possible, therefore, that the potassium supply may influence the amount of chlorophyll formed as well as its activity, although the apparently reciprocal effects of potassium and nitrogen on chlorophyll production [12] tend to introduce an element of doubt in this respect. D. Müller and P. Larsen [13] regard the lowered ratio of assimilation of potassium-deficient plants as being due to "protoplasmic" factors rather than to direct effects on chlorophyll.

In a review of the effects of potassium deficiency on carbon assimilation in plants G. Rohde [14] points out that deficient leaves are smaller, thicker, and more bluish-green than those which are adequately nourished, and that these factors influence the intensity of absorption of light by chlorophyll in regard to total absorption and to the proportional absorption of light of different wave-lengths in the visible spectrum. Willstätter's earlier observations show that in yellow-green leaves (low chlorophyll content) much more carbon dioxide is assimilated per unit chlorophyll than in blue-green (chlorophyll-rich) leaves. In the former, assimilation is probably limited by the proportion of chlorophyll present and in the latter by enzymic activity. Hence, although the importance of potassium in the assimilation process is manifestly great, its apparent direct influence on chlorophyll may in some cases be attributable to secondary effects.

Iron, Manganese, and Magnesium.—It has long been recognised that deficiency of any of these elements may result in chlorotic conditions in plant leaves. Iron and manganese are not constituents of the chlorophyll molecule, but are doubtless concerned in its formation, probably by acting as oxidation–reduction catalysts. In many respects iron and manganese have been shown to differ in their effects on chlorophyll formation.[15] In general, iron has by far the greater stimulative action, although the work of G. B. Ulvin [16] suggests that manganese to some extent supplements the effect of iron. Rohde [17] suggests that the observed effects of manganese in increas-

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[11] *Loc. cit.*; also *Z. Bot.*, 1934, **27**, 257.

[12] *Ann. Reports*, 1935, 438.

[13] *Planta*, 1935, **23**, 501.

[14] *Z. Pflanz. Düng.*, 1936, *A*, **44**, 1.

[15] *Ann. Reports*, 1934, 355.

[16] *Plant Physiol.*, 1934, **9**, 59.

[17] *Loc. cit.*

ing carbon assimilation depend very frequently on the stimulation of the later enzymic stages of the process, although there is little doubt that this element can affect the chlorophyll content of leaves, and probably also its photo-oxidative properties.[18]

The action of iron is much more definitely established. Deficiency of iron leads to chlorosis, but chlorotic plants, the condition of which may be remedied by treatment with iron, do not always show a notably low iron content. Evidently iron may exist in the plant and yet be unable to play its normal part in chlorophyll production. J. Oserkowsky [19] in an attempt to determine the "active" iron finds a general correlation between the chlorophyll content of leaves and the amount of iron extracted by *N*-hydrochloric acid. A small but definite amount of "inactive" iron probably dissolves in the acid. No relationship is apparent between the total and the "active" iron contents or between total iron and chlorophyll contents. Moreover the active iron within the leaf is not all in a water-soluble condition. Prolonged iron deficiency is shown to lead to serious breakdown in the chloroplasts, thus explaining the frequent failure of iron treatment to cure chlorosis when applied late in the season. There is evidence that iron is concerned in the formation of pyrrole compounds, utilised in synthesising the central pyrrole-magnesium nucleus of the chlorophyll molecule. G. Polacci,[20] working with *Chlorella*, observes that the presence of magnesium pyrrole-2-carboxylate in the nutrient medium obviates the necessity of supplying iron. Magnesium supplied as sulphate in an iron-free medium cannot induce chlorophyll production. The apparently catalytic effect of iron on pyrrole ring-formation is not produced if manganese or titanium [21] is used in its place. A. G. P.

A. G. POLLARD.
C. P. STEWART.
J. STEWART.

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[18] K. Noack, *Naturwiss.*, 1926, **14**, 383.

[19] *Plant Physiol.*, 1933, **8**, 449.

[20] *Ber. deut. bot. Ges.*, 1935, **53**, 540; G. Polacci, B. Oddo, and M. Gallotti, *Boll. Soc. ital. Biol. sperim.*, 1935, **10**, 565.

[21] O. L. Inman, G. Barclay, and M. Hubbard, *Plant Physiol.*, 1935, **10**, 821.

ANALYTICAL CHEMISTRY.

The number of papers with a bearing on analysis which have appeared during the period under review has not diminished and the task of selection is no easier. In surveying the literature, however, it has again been noticed that certain papers appear to be devoted to the rediscovery of well-established facts or of methods which are by no means new. It is true that such contributions make a Reporter's task somewhat easier, but with the literature in its over-burdened condition they are surely superfluous.

In this Report a separate section has been devoted to Colorimetry, a branch of analysis which, in recent years, appears to be coming into its own, with a wider future before it. Hence the time seems ripe for a separate treatment of the subject in its quantitative aspect, with especial reference to the instrumental side.

L. S. T.

MAGNETO-OPTIC METHOD OF CHEMICAL ANALYSIS.

An extensive literature [1] has grown round this much-debated method of analysis since it was first launched by Allison in 1930.[2] Subsequently, the method has been the subject of much controversy. Some investigators have claimed success with it, whilst others have reported a complete failure, and not only has the interpretation of the results been in dispute, but also the very existence of the minima has been called in question.

Recently, F. G. Slack [3] has reported a critical investigation of the method, and although minima were observed he regards them as a type of *N*-ray phenomenon, and as such, subject to physiological and psychological effects. Further, with J. A. Peoples, jun.,[4] he reports that attempts to reproduce time-lag measurements and

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[1] Bibliographies which cover the field will be found in the articles by Slack, ref. (3), and by Cooper, ref. (9). The method has been mentioned in these Reports from time to time, see *Ann. Reports*, 1931, **28**, 181; 1932, **29**, 300; 1933, **30**, 349; 1934, **31**, 372; 1935, **32**, 142, a detailed description being given in *Ann. Reports*, 1930, **27**, 203.

[2] F. Allison and E. J. Murphy, *J. Amer. Chem. Soc.*, 1930, **52**, 3796; the first papers on the time-lag in the Faraday effect by Allison appeared in 1927; see J. W. Beams and F. Allison, *Physical Rev.*, 1927, **29**, 161; *Phil. Mag.*, 1927, [vii], **3**, 1199.

[3] *J. Franklin Inst.*, 1934, **218**, 445; cf. also H. W. Farwell and J. B. Hawkes, *Physical Rev.*, 1935, [ii], **47**, 78.

[4] *Ibid.*, 1934, [ii], **45**, 126.

chemical analyses have failed. Working independently, H. G. MacPherson [5] finds himself in substantial agreement with Slack and Farwell and Hawkes, and is unable to confirm sharp minima characteristic of the substance under investigation. More evidence of a similar nature comes from M. A. Jepperson and R. M. Bell.[6] On the other hand, G. Hughes and R. Goslin [7] seem to have made a pertinent reply to many of these doubts and misgivings by demonstrating the reality and reproducibility of the minima photographically, and they claim that these objective tests are characteristic of the inorganic acids and salts which they have examined. Furthermore, G. M. Wissink and J. W. Woodrow [8] have such confidence in the method that they use it to detect vitamin-A, to the presence of which they attribute the characteristic minimum given by many animal and vegetable products.

Finally, we have a recent series of articles by S. S. Cooper and T. R. Ball [9] who, after a somewhat enthusiastic introduction, in which they describe the magneto-optic apparatus as " perhaps the most important tool for chemical research developed in the past decade " and extol the advantages of this method of analysis, proceed in the first paper to deal with the history and present status of the method. From their review they believe conclusively that the minima do exist and that they are characteristic of the substance or substances under investigation. The second paper discusses in some detail the construction, arrangement, and adjustment of the apparatus, and describes a successful test of the method in solving a series of unknowns, whilst the last paper gives the actual procedure used in locating the minima for a specific example, *viz.*, salicylic acid. The authors' concluding remarks are illuminating and make it clear that the technique is difficult, whilst a long and very specialised training is necessary before success in the use of the method can hope to be achieved. It would seem, therefore, that for the present at least the practising analyst will still have to rely on the more purely chemical methods which are at his disposal for the identification and determination of small concentrations of unknowns.

L. S. T.

INORGANIC ANALYSIS.

Quantitative.

Standards for Volumetric Analysis.—In last year's Report (p. 452) this subject was dealt with in some detail. The stabilisation of

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[5] *Physical Rev.*, 1935, [ii], **47**, 310.

[6] *Ibid.*, p. 546.

[7] *Ibid.*, p. 317.

[8] *Ibid.*, 1934, [ii], **45**, 126.

[9] *J. Chem. Educ.*, 1936, **13**, 210, 278, 326; cf. also T. R. Ball, *Physical Rev.*, 1935, [ii], **47**, 548.

$0{\cdot}1N$-sodium thiosulphate solutions by the addition of borax was mentioned. Now it is pointed out[10] that such solutions give, in neutral solution, iodine values which are too low even when only one-twelfth of the usual amount of crystalline borax is added.

Experimental work indicating the suitability of borax as an acidimetric standard appears from time to time, but the methods adopted for drying the hydrated salt have probably prevented its more extended use. Drying by alcohol and ether is now shown to be an easy and satisfactory procedure which eliminates this disadvantage.[11] Further, loss of water by exposure to air is not a serious source of error over periods of less than a week or ten days.

I. M. Kolthoff and J. J. Lingane[12] have shown that potassium thiocyanate is a suitable standard for work of ordinary accuracy (± 0·1%), and when stored in the dark the pure, melted salt is stable indefinitely; deliquescence, moreover, is harmless at a relative humidity of less than 45%. When protected from light, aqueous solutions gave no detectable change in titre after eleven months' storage.[13] In spite of their high precision or reproducibility, potentiometric titrations of silver with thiocyanate are not suited to work of a highly exact nature, owing to side reactions which have been found to take place, and the relatively good results obtainable with the Volhard method are due, as is often the case in an analytical process, to a compensation of errors.[12]

G. F. Smith, V. R. Sullivan, and G. Frank[14] have proposed the salt $(NH_4)_2Ce(NO_3)_6$, which, incidentally, is indicated to be the complex ammonium hexanitratocerate, as a reference substance in ceriometry. They have worked out an easy method of preparation in a degree of purity sufficient for this purpose and have shown that the stability of the salt in hot, dilute sulphuric acid is satisfactory. Many desirable properties are claimed for the new standard, and its use may well prove to be a definite advance in volumetric work.

Indicators.—There is now available a wide range of indicators suitable for the titration of acids and bases, but in those of the newer oxidation–reduction type there is still room for improvement and a widening in scope. As time goes on this extension is gradually being made, and one of the latest additions offering promise of wide use is phenylanthranilic acid which has now been recommended[15] for many of the usual oxidation processes of volumetric analysis,

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[10] P. Horkheimer, *Pharm. Ztg.*, 1935, **80**, 1330.

[11] F. Hurley, jun., *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 220.

[12] *J. Amer. Chem. Soc.*, 1935, **57**, 2126.

[13] Cf., however, E. N. Taran, *J. Gen. Chem. Russia*, 1935, **5**, 602.

[14] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 449.

[15] A. Kirssanov and V. Tscherkassov, *Bull. Soc. chim.*, 1936, [v], **3**, 817; W. S. Syrokomsky and V. V. Stiepin, *J. Amer. Chem. Soc.*, 1936, **58**, 928.

especially for titrations with ceric sulphate. It gives, it is claimed, a sharp, reversible colour change and is more stable in the presence of excess of oxidant than diphenylamine and its derivatives; the oxidation potential is + 1·08 volts and the indicator error is negligible. In iron titrations the addition of phosphoric acid is no longer necessary, and the ease with which it can be prepared gives it a decided advantage over the costly *o*-phenanthroline compound.

A 1% solution of brucine in 3*N*-sulphuric acid is another indicator of this type which presents possibilities, and has been described as a suitable internal indicator for iron in dichromate titrations.[16] The colour change from green to red is said to be more distinct than that of diphenylamine and to be unaffected by ferric ions in large excess, by mercury, and by stannic ions; here again, phosphoric acid is unnecessary, and permanganate can be used as the titrant with hydrochloric acid present. This indicator has been employed with advantage in the analysis of chromium–iron alloys, or of ores where the concentration of ferric iron is high.

Sodium diphenylbenzidinemonosulphonate and the diphenylamine derivatives, $NHPh{\cdot}C_6H_4{\cdot}SO_3Na$ and $NHPh{\cdot}C_6H_3Me{\cdot}SO_3Na$, have also been described [17] as oxidation–reduction indicators for dichromate titrations.

The details for the successful and accurate use of diphenylcarbazide as an internal indicator in the volumetric determination of iron have been fully worked out,[18] but the close attention to procedure which is demanded, the indicator correction which has to be found, and the careful control which is necessary in the titration itself may restrict the popularity of the method.

The same substance has been satisfactorily applied [19] also to determine the end-point in titrating chloride ion with mercuric nitrate solution.

Benzopurpurin-B and -4B have been put forward as indicators for the bromometric titration of tin and antimony.[20]

The advantages to be gained from the recently-introduced fluorescence indicators are discussed by M. Déribéré, who recommends umbelliferone, β-methylumbelliferone, and uranyl salts (in the absence of halogens) as suitable for strong acids and bases, β-naphthol or eosin-BN for weak acids, and æsculin or fluorescein for weak

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[16] D. S. Narayanamurthi and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 1936, **3**, *A*, 38; S. Miyagi, *J. Soc. Chem. Ind. Japan*, 1933, **36**, 146.

[17] S. Cohen [with R. E. Oesper], *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 364.

[18] H. E. Crossley, *Analyst*, 1936, **61**, 164.

[19] I. Roberts, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 365.

[20] Z. Raichinschtein, *J. Appl. Chem. Russia*, 1935, **8**, 1470.

bases.[21] 1-Naphthol-4-sulphonic acid (Nevile and Winther's acid) shows a sharp change from no fluorescence to an intense blue at p_{H} 6—6·5,[22] and naphthionic acid and Schaeffer's salt give, respectively, changes in fluorescence from p_{H} 3 to 12 and 5 to $>$ 11, by which p_{H} can be measured to 0·5 unit.[23]

In connexion with adsorption indicators, A. J. Berry [24] describes the conditions under which phenosafranine, tartrazine, and rose-Bengal are best adapted to systems such as silver–halogen [25] and thallous–thallic halides, and by titrating nitric or acetic acid with sodium hydroxide in the presence of lead nitrate and fluorescein or eosin, S. N. Roy [26] extends their application to acidimetry. Other indicators worthy of note are a universal indicator for the p_{H} range 1·2—12·7,[27] and 4-nitrocatechol,[28] and oximinothiocamphor, p_{H} range 8·6—9·0,[29] for acidimetry.

The theories of Bjerrum and Brønsted have been applied to the titration of weak acids and bases in water–ethyl alcohol mixtures, and it is found that the titration of weak bases is less practicable than in water, but the salts of weak bases, *e.g.*, alkaloid hydrochlorides, may be titrated with much enhanced accuracy in concentrated aqueous-alcoholic solutions.[30]

Finally, I. M. Kolthoff [31] has discussed possibilities for the further development of acid–base indicators for the measurement of hydrogen-ion activity and concentration, as well of adsorption, oxidation–reduction, and specific indicators for volumetric purposes.[32]

Reagents.—No new reagent * comparable with 8-hydroxyquinoline

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[21] *Ann. Chim. analyt.*, 1936, [iii], **18**, 37.

[22] *Idem, ibid.*, p. 120.

[23] *Idem, ibid.*, p. 173.

[24] *Analyst*, 1936, **61**, 315.

[25] Cf. also R. Ripan-Tilici, *Z. anal. Chem.*, 1936, **104**, 16, for argentometric titration of halide, thiocyanate, selenocyanate, and cyanate with fluorescein as adsorption indicator.

[26] *J. Indian Chem. Soc.*, 1936, **13**, 486; cf. *idem, ibid.*, 1935, **12**, 584.

[27] F. Čůta and K. Kámen, *Chem. Listy*, 1936, **30**, 22, 129.

[28] S. R. Cooper and V. J. Tulane, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 210.

[29] D. C. Sen, *J. Indian Chem. Soc.*, 1935, **12**, 751.

[30] H. Baggesgaard-Rasmussen, *Z. anal. Chem.*, 1936, **105**, 269.

[31] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 237.

[32] For a useful general article see "Universal and Other Indicators," by T. G. Pearson in Thorpe's "Dictionary of Applied Chemistry," 1935, Supplement, Vol. 2, p. 617.

* Styryl dyes (P. Krumholz and E. Krumholz, *Mikrochem.*, 1935, **19**, 47), 8-hydroxy-5-methylquinoline (C. E. Gietz and A. Sá, *Anal. Asoc. Quím. Argentina*, 1935, **23**, 45), a mercaptan-like substance named "thiocarbin" (A. Steigmann, *Phot. Ind.*, 1936, **34**, 499), and what is probably ethyl 5-keto-2-thionhexahydropyrimidine-4-carboxylate (S. E. Sheppard and H. R. Brigham, *J. Amer. Chem. Soc.*, 1936, **58**, 1046) are newly-described reagents for certain metals.

or thionalide has recently come to the fore, but a review which has just been published [33] of the use of organic reagents in both qualitative and quantitative analysis and their increasing significance will be of much interest to all engaged in analytical work.

Gravimetric and Volumetric Methods for the Determination of the Elements.—In a report of this nature it is impossible to do more than mention a comparatively small number of the many papers which have been concerned with the determination of the elements during the period under review, and although all new analytical methods should be approached with an open mind tempered by a critical outlook, any criticisms of the present work would be presumptive and premature, for the true value of a method can be assessed only in relation to the purpose for which it is designed, and after it has been put to the test of practical experience.

Group I. The accuracy of the potentiometric iodide–silver titration as distinct from its precision or reproducibility has been recently investigated.[34] In the slow titration of *silver* with iodide, errors are produced by the adsorption of iodide ions by the silver iodide formed, but the magnitude of the error can be reduced to a small value (0·017% or 0·028%) by titrating at 90°, or by digesting the precipitate at 90° in presence of a slight excess of silver prior to completion of the titration at the ordinary temperature. Silver can also be successfully titrated with potassium iodide, even in the presence of cupric or ferric ions, by using ceric ammonium sulphate and starch as internal indicators, since oxidation of the iodide ion to iodine by $Ce^{\cdot\cdot\cdot\cdot}$ is not permanent until the end-point is reached.[35] Having found that, using the iodine monochloride end-point, the titration of *thallous* salts with either potassium permanganate or ceric sulphate is unreliable, E. H. Swift and C. S. Garner [36] recommend titration with potassium iodate instead.

The method previously described [37] for the removal of *tungsten* from tin by means of 8-hydroxyquinoline in an oxalate medium gives high results for tungsten owing to retention of tin, and a modification now put forward [38] is designed to overcome this.

Group II. Further details [39] have now been supplied [40] concerning

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[33] F. Feigl, *Ind. Eng. Chem. (Anal.)*, 1936, **8**, 401.

[34] I. M. Kolthoff and J. J. Lingane, *J. Amer. Chem. Soc.*, 1936, **58**, 1524; cf. *idem, ibid.*, p. 1528. See *idem, ibid.*, 1935, **57**, 2126, 2377, for similar studies of the systems silver–thiocyanate and mercury–thiocyanate.

[35] A. Bloom and W. M. McNabb, *Ind. Eng. Chem. (Anal.)*, 1936, **8**, 167.

[36] *J. Amer. Chem. Soc.*, 1936, **58**, 113.

[37] A. Jílek and A. Ryšánek, *Coll. Czech. Chem. Comm.*, 1933, **5**, 136.

[38] *Idem, ibid.*, 1936, **8**, 246.

[39] Cf. *Ann. Reports*, 1935, **32**, 457.

[40] G. Spacu and M. Kuraš, *Z. anal. Chem.*, 1936, **104**, 88.

the gravimetric determination of *lead, thallium, bismuth,* and *gold,* which are precipitated by thiolbenzthiazole as $C_7H_4NS_2PbOH$, $C_7H_4NS_2Tl$, $(C_7H_4NS_2)_3Bi$, and $(C_7H_4NS_2)_3Au$, respectively; and lead has been separated as carbonate, from copper, or cobalt and nickel, by the passage of carbon dioxide into a solution of the nitrates in presence of pyridine.[41] After a critical review of the determination of lead as sulphate, and of *antimony* as sulphide by the method of Vortmann and Metzl,[42] modifications of procedure have been recommended for these metals and their alloys.[43] The chromate method for lead has received further investigation,[44] and the B.P. (1932) method has been criticised as inaccurate owing to the non-quantitative liberation of oxalic acid from the lead oxalate precipitate; more accurate results are obtained, it is stated, by determination of the excess of oxalic acid in the filtrate.[45]

In the gravimetric determination of *mercury,* mercuric sulphide is removed from the weighed sulphide–sulphur precipitate by dissolution in cold, concentrated hydriodic acid and the residual sulphur is weighed. The procedure can conveniently be applied to the rapid evaluation of technical grades of the sulphide.[46] An indirect volumetric method, based on a critical study of the dichromate–pyridine method of G. Spacu and J. Dick,[47] consists of titrating the dichromate ion in the precipitated $[Hg\,py_2]Cr_2O_7$ by one of the conventional methods, whilst substitution of acetone, in which the complex is less soluble than in alcohol, simplifies and improves the washing technique originally advocated by Spacu and Dick.

A critical comparison of a number of methods by an independent worker often serves a useful purpose in assessing the true value of proposed methods and helps to clarify the position for those seeking an alternative to the older methods available. Several such reviews have been published during the year. Various separations of *bismuth* from lead, *viz.*, bromide–bromate hydrolysis,[48] the pyrogallol precipitation,[49] and the cupferron method,[50] have now been

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[41] A. Jílek, J. Kot'a, and J. Vřešt'al, *Chem. Listy*, 1935, **29**, 299.

[42] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," 1935, Vol. II, p. 220.

[43] H. Vdoviszevski, *Z. anal. Chem.*, 1936, **104**, 94.

[44] *Idem, ibid.*; L. Guzelj, *ibid.*, p. 107; Z. Karaoglanov and M. Michov, *ibid.*, 1935, **103**, 113.

[45] S. Wetherell, *Quart. J. Pharm.*, 1935, **8**, 453.

[46] E. R. Caley and M. G. Burford, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 43.

[47] *Z. anal. Chem.*, 1929, **76**, 273.

[48] L. Moser and W. Maxymowicz, *Z. anal. Chem.*, 1925, **67**, 248.

[49] F. Feigl and H. Ordelt, *ibid.*, **65**, 448.

[50] A. Pinkus and J. Dernies, *Bull. Soc. chim. Belg.*, 1928, **37**, 267.

checked,[51] but the hydrolysis in formic acid solution [52] leads to irregular results. Bismuth can also be separated from copper by a modification of the cyanide method of Fresenius and Haidlen,[53] but for both the bismuth-lead and the bismuth–copper separations the bromide–bromate procedure of Moser and Maxymovicz is preferred. L. Kielt and G. C. Chandlee [54] find that precipitation with gallic acid at 70° serves to separate bismuth from lead, copper, cadmium, and many other metals, but not from mercury, antimony, tin, or silver. The phosphate method has also been re-examined [55] and found to be inaccurate when lead is present. F. Hecht and R. Reissner [56] report that the micro-determination of bismuth as oxyiodide [57] is inexact, and that the macro-determination as $C_9H_6N{\cdot}OH,HBiI_4$ [58] is unsatisfactory owing, *inter alia*, to the partial decomposition of the precipitate during washing.[59] Good results on both the macro- and the micro-scale can be obtained, however, under the exact conditions prescribed, by precipitation with 8-hydroxyquinoline.

The well-known Haën–Low volumetric method for *copper* is accurate but long, and a shortening of the time required is much to be desired. B. Park's procedure [60] which aims at effecting this has now been modified; [61] potassium hydrogen phthalate has no material effect on the p_H of the solution and can be omitted, but in order to ensure complete oxidation of an ore containing sulphide, iron, and arsenic, a double treatment with nitric and hydrochloric acids, or a single treatment with the two acids followed by one with saturated bromine-water, is found to be essential. H. W. Foote and J. E. Vance [62] apply their modified iodometric method,[63] with controlled p_H, to determine copper in the presence of As^V and not more than approximately 20 mg. of antimony, interference by iron being prevented by the now common device of adding sodium fluoride.*

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[51] E. A. Ostroumov, *Z. anal. Chem.*, 1936, **106**, 36.

[52] A. L. Benkert and E. F. Smith, *J. Amer. Chem. Soc.*, 1896, **18**, 1055.

[53] See Treadwell and Hall, *op. cit.*, p. 206.

[54] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 392.

[55] W. C. Blasdale and W. C. Parle, *ibid.*, p. 352.

[56] *Mikrochem.*, 1935, **18**, 283.

[57] R. Strebinger and W. Zins, *Mikrochem.*, 1927, **5**, 166; *Z. anal. Chem.*, 1927, **72**, 417.

[58] R. Berg and O. Wurm, *Ber.*, 1927, **60**, 1664.

[59] F. Hecht and R. Reissner, *Z. anal. Chem.*, 1935, **103**, 261; see also, *idem, ibid.*, pp. 88, 186.

[60] *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 77.

[61] W. R. Crowell, T. E. Hillis, S. C. Rittenberg, and R. F. Evenson, *ibid.*, 1936, **8**, 9.

[62] *Ibid.*, p. 119. [63] *Ann. Reports*, 1935, **32**, 459, ref. (73).

* See K. Heller and F. Machek (*Mikrochem.*, 1936, **19**, 147), for a review of the literature on the determination and detection of cadmium.

The complete precipitation of *molybdenum* by hydrogen sulphide is generally a matter of difficulty in an analysis, and it is noteworthy that the trisulphide can be precipitated quantitatively in the presence of formic acid by initial reaction with a solution of hydrogen sulphide saturated at 0°,[63a] a finding which supports previous claims of a similar nature;[64] separation from tungsten is accomplished by adjusting the p_H to 2·9 by means of a suitable buffer. There is little to be gained, in general, by conducting the precipitation of the molybdenum under pressure—another point which has been much disputed in the past. According to H. Goto,[65] molybdenum is completely precipitated by 8-hydroxyquinoline in the range p_H 3·3—7·6, and vanadium at p_H 2·7—6·1 : and the conditions under which the former can be determined volumetrically by oxidation of Mo^V to Mo^{VI} with 0·1N-ammonium vanadate have been investigated by R. Lang and S. Gottlieb;[66] iron, vanadium, and large amounts of copper render the method impracticable. N. H. Furman and W. M. Murray, jun.,[67] reduce Mo^{VI} quantitatively to Mo^V by shaking with mercury in a solution which is 2—3·5N with respect to hydrochloric acid, and titrate the quinquivalent molybdenum with ceric sulphate at the ordinary temperature using the *o*-phenanthroline–ferrous complex indicator. They state that the presence of considerable quantities of phosphate, arsenate, or of ammonium salts is without effect on the accuracy of the molybdenum determination.

A fractional distillation method has been worked out at the Bureau of Standards for the separation of *arsenic*, *antimony*, and *tin* from one another and from elements having non-volatile chlorides; germanium and rhenium, but not bismuth, interfere.[68] The optimum conditions of acidity for the volumetric determination of antimony and arsenic by Andrews's iodine monochloride method [69] have been fully investigated,[70] and a critical examination of various methods for arsenic in iron, steels, and iron ores has shown that the best results are obtained by dissolution in nitric acid or bromine-water (bromine and hydrochloric acid for ores) followed by distillation of the arsenic as chloride.[71] Published methods for the Gutzeit reaction carried out on paper strips have also been critically reviewed.[72]

[63a] H. Yagoda and H. A. Fales, *J. Amer. Chem. Soc.*, 1936, **58**, 1494.

[64] Cf. I. Koppel, *Chem.-Ztg.*, 1924, **48**, 801; J. Štěrba-Böhm and J. Vostřebal, *Z. anorg. Chem.*, 1920, **110**, 81.

[65] *J. Chem. Soc. Japan*, 1935, **56**, 314.

[66] *Z. anal. Chem.*, 1936, **104**, 1.

[67] *J. Amer. Chem. Soc.*, 1936, **58**, 1689.

[68] J. A. Scherrer, *J. Res. Nat. Bur. Stand.*, 1936, **16**, 253.

[69] *J. Amer. Chem. Soc.*, 1903, **25**, 756.

[70] A. Mutschin, *Z. anal. Chem.*, 1936, **106**, 1.

[71] A. Stadeler, *Arch. Eisenhüttenw.*, 1935—36, **9**, 423.

[72] W. Mühlsteph, *Z. anal. Chem.*, 1936, **104**, 333.

Dry distillation in oxygen serves to separate 0·1—0·001% of *selenium* from sulphur and sulphur-containing materials.[73] Arsenic and tellurium present in an amount equivalent to the selenium do not interfere.[74]

Volumetric methods for *tin* have long been a source of tribulation to the analyst, and two papers which have recently been published may help to clear the situation. According to F. L. Okell and J. Lumsden,[75] low results in tin titrations are due to oxygen dissolved in the iodine solution and not necessarily to incomplete exclusion of air in the flask, and the interfering action of titanium experienced in the analysis of tin ores is eliminated when oxygen-free iodine is used for titration. Reduction with aluminium turnings is recommended in ore analysis.[76] For alloys of tin and lead with less than 2% of antimony, the tin and lead are best dissolved directly in concentrated hydrochloric acid in absence of oxygen, and the antimony removed by filtration before titration with potassium iodate. Removal of antimony is essential since cold stannic chloride reacts with freshly-precipitated antimony too rapidly to permit accurate titration of $Sn^{\cdot\cdot}$ in its presence.[77] The titration of $Sn^{\cdot\cdot}$ has also been carried out with ceric sulphate, diphenylamine being the indicator.[78]

When heated at 400—500° with excess of ammonium iodide, tin dioxide is quantitatively volatilised as stannic iodide and advantage can be taken of this to ascertain the purity of the ignited metastannic acid obtained in the usual course of an analysis.[79]

R. Gilchrist and E. Wichers have made an important contribution to the analysis of the *platinum metals* in which a new procedure for the separation of osmium, ruthenium, platinum, palladium, rhodium, and iridium from one another, and their gravimetric determination, have been described;[80] no specialised equipment or reagents are necessary and an accuracy comparable with that of the best analytical procedures for the common metals is claimed for their methods.

Group III. For the determination of small amounts of *iron*, *aluminium*, and *titanium* in admixture, 8-hydroxyquinoline and its 5 : 7-dibromo-derivative, which precipitates titanium in acid and aluminium in alkaline solution, have been utilised.[81] J. Dewar and

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[73] See G. G. Marvin with W. C. Schumb, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 109, for determination of selenium in 18 : 8 stainless steels.

[74] *Idem, ibid.*, 1935, **7**, 423.

[75] *Analyst*, 1935, **60**, 803.

[76] See also L. Deutsch, *Ann. Chim. analyt.*, 1936, [iii], **18**, 10.

[77] H. F. Hourigan, *Analyst*, 1936, **61**, 328.

[78] N. A. Rudnev, *Trans. Butlerov Inst. Chem. Tech. Kazan*, 1934, No. 2, 51.

[79] E. R. Caley and M. G. Burford, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 114.

[80] *J. Amer. Chem. Soc.*, 1935, **57**, 2565.

[81] A. M. Zanko and A. J. Bursuk, *J. Appl. Chem. Russia*, 1936, **9**, 895.

P. A. Gardiner [82] find that, contrary to the adverse criticism of L. Moser and M. Niessner,[83] a slight modification of H. Britton's method [84] (hydrolysis of the alkali beryllate) furnishes an accurate separation of aluminium and beryllium when the former is not greatly in excess of the latter. For the case of aluminium and zinc, F. H. Fish and J. M. Smith, jun., adopt the aluminate method,[85] in which aluminium is weighed as $2Li_2O,5Al_2O_3$, zinc being determined in the filtrate as the pyrophosphate, whilst T. Kôzu [86] separates aluminium from manganese, cobalt, and nickel, but not zinc, by precipitation with a saturated, aqueous solution of aniline, the aluminium being weighed as the oxide.

This use of organic bases in preference to ammonia is extending,[87] and 20% pyridine is now employed to precipitate *iron*, *chromium*, and *aluminium* as hydroxides from dilute nitric or hydrochloric acid solution in the presence of the corresponding ammonium salts. A single precipitation is said to give a separation, which is practically complete, from manganese, cobalt, and nickel, but not zinc, and the method has been applied to pyrolusite and to cobalt ores.[88] *Uranium*, also, is precipitated, as $H_2U_2O_7$, from solutions of uranyl salts, thus providing a quantitative separation from the alkaline earths.[89]

For the removal of *gallium* from beryllium, titanium, zirconium, and thorium, S. Ato [90] has recourse to the ether-extraction method from hydrochloric acid solution, and finally precipitates the gallium with sodium camphorate; and for the determination of this metal in aluminium, J. A. Scherrer [91] adopts the same device but precipitates the gallium with cupferron and then ignites it to the oxide, after removal of any iron, tin, etc., which has accompanied the gallium into the ether extract. An alternative method, obviating an extraction and based on precipitation with cupferron in sulphuric acid solution, is also given.

In view of the use which is made in some laboratories of perchloric acid as an oxidising agent for *chromium*, it is of interest to learn that the incomplete oxidation which results when this acid alone is used is due to the production of a small amount of hydrogen peroxide;

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[82] *Analyst*, 1936, **61**, 536.

[83] *Monatsh.*, 1927, **48**, 113.

[84] *Analyst*, 1921, **46**, 361, 437; 1922, **47**, 50.

[85] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 349; see J. T. Dobbins and J. P. Sanders, *J. Amer. Chem. Soc.*, 1932, **54**, 178.

[86] *J. Chem. Soc. Japan*, 1935, **56**, 562, 683.

[87] See *Ann. Reports*, 1935, **32**, 462, ref. (10); 460, ref. (86).

[88] E. A. Ostroumov, *Z. anal. Chem.*, 1936, **106**, 170.

[89] *Idem, ibid.*, p. 244.

[90] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 71; cf. *ibid.*, 1934, **24**, 270; 1931, **15**, 289.

[91] *J. Res. Nat. Bur. Stand.*, 1935, **15**, 585.

quantitative results, however, are obtained with a mixture of perchloric and sulphuric acids in certain proportions.[92]

Analytical methods for the determination of *zirconium* and the complete analysis of zirconium minerals have been reviewed.[93]

W. R. Schoeller and his collaborators have now completed their investigations into the analytical chemistry of *tantalum*, *niobium*, and their mineral associates : the four papers recently published complete the series. In the first of these,[94] the fate of beryllium in the more important operations advocated for the separation of the various earths and the analysis of minerals containing them is dealt with; the second [95] is concerned with the determination of tungsten in earth-acid minerals,[96] and the third with the separation of phosphorus and vanadium.[97] The last paper [98] contains a general summary which is intended as a key to facilitate the study of the whole series. Not the least striking feature of these remarkable investigations is the simplicity of the apparatus and reagents whereby the results have been achieved; and, as is pointed out in the final paper, "the simple classic processes of mineral analysis have proved adequate for the solution of some of its most difficult problems." The monograph based on these researches, which is to be published under the ægis of the Society of Public Analysts, will be awaited with great interest by all whose work takes them into the field of mineral analysis.

Anthranilic acid has been confirmed as a suitable, although restricted, reagent for the determination of *zinc*, cadmium, cobalt, nickel, and copper; the conditions specified by H. Funk and M. Ditt [99] are satisfactory except in the case of nickel, and are not improved by the addition of ammonium or sodium acetate, or sodium tartrate.[99a] This acid, in the form of its sodium salt, has also been employed for the micro-determination of zinc.[1]

The post-precipitation of zinc sulphide with mercuric sulphide has been studied in its theoretical and practical aspects by I. M. Kolthoff and R. Moltzau ;[2] and J. R. Caldwell and H. V. Moyer [3] find

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[92] G. F. Smith, L. D. McVickers, and V. R. Sullivan, *J. Soc. Chem. Ind.*, 1935, **54**, 369T.

[93] G. A. Ampt, *J. Proc. Austral. Chem. Inst.*, 1935, **2**, 321.

[94] W. R. Schoeller and H. W. Webb, *Analyst*, 1936, **61**, 235.

[95] W. R. Schoeller and E. F. Waterhouse, *ibid.*, p. 449.

[96] Cf. *Ann. Reports*, 1935, **32**, 462, ref. (21).

[97] W. R. Schoeller and H. W. Webb, *Analyst*, 1936, **61**, 585.

[98] W. R. Schoeller, *ibid.*, p. 806.

[99] *Z. anal. Chem.*, 1933, **93**, 241.

[99a] R. J. Shennan, J. H. F. Smith, and A. M. Ward, *Analyst*, 1936, **61**, 395.

[1] C. Cimerman and P. Wenger, *Arch. Sci. phys. nat.*, 1935, [v], **17**, Suppl., 94—98.

[2] *J. Physical Chem.*, 1936, **40**, 779.

[3] *J. Amer. Chem. Soc.*, 1935, **57**, 2372.

that the addition of small amounts of gelatin or agar produces immediate and complete flocculation of zinc sulphide suspensions and permits filtration 15 minutes after precipitation. Satisfactory separations from nickel, manganese, aluminium, or chromium can thus be obtained,[4] and when a small amount of acraldehyde is also added, a good separation from cobalt can be effected with a single precipitation.[5]

Group IV. Precipitation is generally preferable to extraction from solids in quantitative work, and one such method has been worked out [6] for the nitrates of the alkaline-earth metals. *Strontium* nitrate is completely precipitated in a dense, crystalline form and separated from numerous other metals by the addition of 100% nitric acid until the resultant solution contains not less than 79% of nitric acid. *Barium* and lead can be obtained free from other metals in a similar way. The solubility of calcium nitrate decreases rapidly with increasing acid concentration, and *calcium* and strontium nitrates are separated from each other when the content of nitric acid lies between 79 and 81% : the method seems preferable to that of S. G. Rawson.[7] Attempts to separate these two metals by precipitation of strontium nitrate with nitric acid in various organic media were not encouraging.

Rosolic acid has been used as indicator for the direct titration of *barium* with potassium chromate by the method of K. Jellinek and J. Czerwinski,[8] and this furnishes an indirect method for the determination of sulphate and of sulphur in pyrites and slags.[9]

Group V. The determination of *potassium* on the micro-scale forms the subject of a detailed examination by P. Wenger, C. Cimerman, and C. J. Rzymowska,[10] who find that Emich's chloroplatinate method gives good results for this element alone, but not in the presence of more than four times as much sodium. By an adaptation of the macro-method of F. G. Smith and J. L. Gring,[11] in which potassium is converted into its perchlorate before treatment with chloroplatinic acid, they have been able to determine gravimetrically amounts of potassium of the order of 0·5 mg. in the presence of ten

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[4] *Idem, J. Amer. Chem. Soc.*, 1935, **57**, 2372.

[5] *Idem, ibid.*, p. 2375.

[6] H. H. Willard and E. W. Goodspeed, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 414.

[7] *J. Soc. Chem. Ind.*, 1897, **16**, 113; cf. W. Noll, *Z. anorg. Chem.*, 1931, **199**, 193.

[8] *Z. anorg. Chem.*, 1923, **130**, 253.

[9] A. V. Vinogradov, *Ann. Chim. analyt.*, 1935, [iii], **17**, 285.

[10] *Mikrochem.*, 1936, **20**, 1; *Arch. Sci. phys. nat.*, 1935, [v], **17**, Suppl., p. 89.

[11] *J. Amer. Chem. Soc.*, 1933, **55**, 3957.

times as much sodium. A volumetric ending, which is particularly suitable in the determination of potassium in biological media, has also been worked out by these authors, and depends on the conversion of the K_2PtCl_6 into K_2PtI_6 by treatment with potassium iodide, and titration of the iodoplatinate with thiosulphate.[12]

C. H. Greene [13] has examined the sensitivity of the magnesium uranyl acetate reagent to sodium and potassium, and his data show that addition of alcohol increases the sensitivity of the reagent towards sodium more than towards potassium—a desirable result. The distinction between these two metals also improves as the ratio of the volume of the reagent to that of the test solution is increased. Errors arising from the micro-determination of sodium by means of an aqueous-alcoholic solution of this reagent have also been discussed by A. Krassilchik,[14] who puts forward an improved technique.

Disturbing discrepancies have often come to light in the values obtained for the alkalis by independent analysts using the Lawrence Smith method on the same material, and incomplete attack in the fusion may often be the explanation of the disagreement. This and other sources of error are discussed by M. O. Lamar, W. M. Hazel, and W. J. O'Leary,[15] who suggest remedies and improvements particularly for substances known to be refractory. For aluminium refractories, other workers [16] fuse with ammonium fluoride as a method of attack, and then, after expulsion of hydrogen fluoride, precipitate the sodium with zinc uranyl acetate, reduce the uranium in the precipitate by a coil of aluminium, and titrate back with permanganate. For amounts of sodium (? Na_2O) from 0·6 to 4·5%, test results show good agreement with those obtained by the Lawrence Smith method.

Anions. There remain to be mentioned in this section some investigations concerned with the determination of the anions.

According to G. L. Jenkins and C. F. Bruening,[17] the official (National Formulary) methods are suitable for ferric but not for ammonium, calcium, sodium, potassium, and manganese *hypophosphites*,[18] and improvements are suggested. H. Terlet and

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[12] For a "Sammelreferat" of methods for the micro-determination of potassium, see C. Cimerman and C. J. Rzymowska, *Mikrochem.*, 1936, **20**, 129.

[13] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 399.

[14] *Compt. rend.*, 1936, **203**, 78.

[15] *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 429.

[16] H. V. Churchill, R. W. Bridges, and A. L. Miller, *ibid.*, 1936, **8**, 348.

[17] *J. Amer. Pharm. Assoc.*, 1936, **25**, 19.

[18] For these last five salts the methods are based on oxidation to phosphate with nitric acid, precipitation of phosphate with excess of silver nitrate, and a back-titration with ammonium thiocyanate.

A. Briau[19] report that for phosphoric acid Scheffer's method,[20] which consists in the titration of ammonium phosphomolybdate with sodium hydroxide in the presence of formaldehyde, is trustworthy and accurate when steps are taken to remove co-precipitated molybdic acid. They outline procedures for the examination of natural and artificial phosphates of various kinds.[21]

The conditions necessary for the precipitation of benzidine sulphate (p_H 2—3),[22] the titration of *sulphate* with lead nitrate with eosin as indicator,[23] and indirect methods with sodium rhodizonate[24] and rosolic acid as indicators[25] have also been communicated.

Much of the work recently done on the determination of *fluorine* is concerned with H. H. Willard and O. B. Winter's distillation method[26] and suggested modifications of it,[27] and also with Sanchis' method.[28] Owing to the marked adsorption properties of lanthanum fluoride, determination of fluorine by precipitation in this form[29] is found to be impracticable.[30] Precipitation as PbFBr[31] or as K_2SiF_6[32] forms the basis of gravimetric or volumetric methods; and for the determination of fluorine in minerals, calcium fluoride protected as a colloid with gelatin forms the basis of a nephelometric method.[33] A review of various procedures for *silica* in the presence of fluorine has also been made.[34]

When iodine monochloride solution is treated with saturated potassium bromide, iodine is at first liberated, but on addition of more bromide this disappears, iodine bromide being re-formed.

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[19] *Ann. Falsif.*, 1935, **28**, 546.

[20] *J. Officiel*, 1934, Aug. 30th.

[21] See H. Trapp, *J. pr. Chem.*, 1935, [ii], **144**, 93, for calcium phosphates.

[22] E. C. Owen, *Biochem. J.*, 1936, **30**, 352.

[23] J. E. Ricci, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 130.

[24] R. Strebinger and L. von Zombory, with L. Pollák, *Z. anal. Chem.*, 1936, **105**, 346.

[25] A. V. Vinogradov, *loc. cit.*, ref. (9), p. 444.

[26] *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 7.

[27] D. Dahle and H. J. Wichmann, *J. Assoc. Off. Agric. Chem.*, 1936, **19**, 313, 320; D. S. Reynolds, J. B. Kershaw, and K. D. Jacob, *ibid.*, p. 156; W. K. Gilkey, H. L. Rohs, and H. V. Hansen, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 150; W. D. Armstrong, *ibid.*, p. 384 (micro-method).

[28] E. H. Ducloux, *Anal. Asoc. Quim. Argentina*, 1935, **23**, 63; J. M. Muñoz, *Rev. Soc. Argentin. Biol.*, 1934, **10**, 395; A. H. de Carvalho, *Rev. Chim. pura appl.*, 1936, [iii], **11**, 99.

[29] Cf. R. J. Meyer and W. Schulz, *Z. angew. Chem.*, 1925, **38**, 203.

[30] J. Fischer, with E. Müller and H. Knothe, *Z. anal. Chem.*, 1936, **104**, 344.

[31] A. A. Vasiliev, *J. Appl. Chem. Russia*, 1936, **9**, 747; see also, *idem*, *ibid.*, p. 943, for the determination of fluorine in the presence of beryllium.

[32] A. A. Vasiliev, with N. N. Martianov, *Z. anal. Chem.*, 1935, **103**, 107.

[33] R. E. Stevens, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 248.

[34] S. S. Korol and V. M. Kalushskaja, *J. Appl. Chem. Russia*, 1936, **9**, 148.

To apply the iodine bromide process to the determination of *iodine* or *iodide*, the sample is treated with a large excess of potassium bromide, and concentrated hydrochloric acid. After dilution and addition of carbon tetrachloride, the solution is titrated with potassium iodate—other oxidising agents such as ceric sulphate, potassium periodate, permanganate, or dichromate can be used—until the carbon tetrachloride is decolorised. Antimony in the presence of a hydrochloric acid concentration too great for the iodine monochloride process to be satisfactory can also be determined by this means.[35]

Iodides can be titrated with ceric sulphate to a visual end-point in the presence of acetone and sulphuric acid, *o*-phenanthroline–ferrous ion being used as indicator: moderate amounts of chloride have no adverse effect, and interference due to bromide can be largely eliminated by appropriate dilution.[36] Other methods for *bromide* and chloride,[37] and *bromine* and *iodine* in the presence of each other,[38] have also been given.

The use of mercury[39] or amalgams seems to be increasing in popularity in analytical work, and advantage has been taken[40] of the reduction of *chlorates*, *bromates*, and *iodates* by zinc amalgam or by Wood's alloy for their determination.

Vanadous sulphate serves for the quantitative reduction of chlorates, *nitrates*, and *persulphates* in an inert atmosphere, the excess VSO_4 being titrated with potassium permanganate.[41] M. B. Donald reports that the optimum conditions for the reduction of nitrates are very different from those originally specified by Devarda, much less sodium hydroxide being required.[42]

A routine method, based on the " partition " of boric acid between water and ether in the presence of hydrochloric acid and ethyl alcohol, has been developed for the determination of *boron* in glass.[43] Boric oxide contents varying from 0·7 to 16% can be rapidly determined with no material sacrifice of accuracy; zinc interferes seriously, but barium, fluorine, and abnormal amounts of iron only slightly.

Phosphoric acid (40%) has been recommended for the expulsion

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[35] R. Lang, *Z. anal. Chem.*, 1936, **106**, 12.

[36] D. Lewis, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 199.

[37] G. G. Longinescu and E. I. Prundeanu, *Bull. Acad. Sci. Roumaine*, 1935, **17**, 47.

[38] L. Spitzer, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 465.

[39] Cf. N. H. Furman and W. M. Murray, jun., *loc. cit.*, ref. (67), p. 440.

[40] P. G. Popov, *Ukrain. Chem. J.*, 1935, **10**, 413.

[41] P. C. Banerjee, *J. Indian Chem. Soc.*, 1936, **13**, 301.

[42] *Analyst*, 1936, **61**, 249.

[43] F. W. Glaze and A. N. Finn, *J. Res. Nat. Bur. Stand.*, 1936, **16**, 421.

of carbon dioxide from carbonates.[44] This is by no means new, for the use of this acid was advocated over 30 years ago by G. T. Morgan,[45] and since that time many hundreds of determinations of carbon dioxide in dolomite and rocks, for which it is particularly suitable, have been carried out by this means in the laboratory to which the Reporter is attached. It is surprising that the method is not more widely adopted, for it has many advantages, chief among which are the elimination of the condenser and absorption tube necessitated by the volatility of hydrochloric acid, and the very small " blank " which it affords.

Miscellaneous. The preparation of a solution of manganic sulphate as a reagent for volumetric work has been recently described.[46] When protected from light the solution showed no change in titre over a period of nine days, and it rapidly oxidises nitrites, oxalates, ferrous iron in presence of chloride, and V^{II} to V^{V}. The reactions are stoicheiometric, and the end-points well-defined, thus affording results superior to titrations with permanganate.

There are many signs in the literature that more attention is being paid to the statistical evaluation of the possible errors to which an analysis is subject. In the past, this has generally been taken into account in the determination of atomic weights, but it has been somewhat neglected in ordinary analytical work, and this interest which is being displayed in the theoretical aspect of the reliability of an analytical measurement is all to the good. It is also desirable that there should be a clear recognition of the meaning of the terms error, precision, and accuracy, which have often been too vaguely used. An interesting chapter on this subject is to be found in I. M. Kolthoff and E. B. Sandell's recently published book on analysis,[47] and an article which should be of much interest to analysts has been written by A. A. Benedetti-Pichler [48] who discusses the statistical aspects of chemical measurements applicable to analytical data.

Qualitative.

Methods for the Detection of Anions and Cations.—During the period under review several new schemes for the systematic separation of *anions* have been put forward,[49] as well as methods for the commoner

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[44] F. Vojíř, *Chem. Listy*, 1935, **29**, 185.

[45] *J.*, 1904, **85**, 1004.

[46] A. R. J. P. Ubbelohde, *J.*, 1935, 1605.

[47] " Text-book of Quantitative Inorganic Analysis," Macmillan, New York, 1936, Chapter XV, p. 250.

[48] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 373.

[49] E. Umblia, *Keem. Teated*, 1935, **2**, 79; J. T. Dobbins and H. A. Ljung, *J. Chem. Educ.*, 1935, **12**, 586; E. W. Flosdorf and C. Henry, *ibid.*, 1936, **13**, 274; F. Pozna and E. Migray, *Ann. Chim. appl.*, 1936, **26**, 81.

cations which dispense with the use of hydrogen sulphide.[50] A simplified method for Group II [51] has also been recommended.

E. R. Caley and M. G. Burford [52] find that concentrated hydriodic acid is a valuable reagent for the detection and separation of compounds such as lead sulphate, stannic oxide, silver halides, calcium fluoride and fluorspar, and certain chromium compounds, which help to form the " insolubles " of qualitative analysis. Reactions are often distinctive and frequently more rapid and convenient than a fusion, and some of the separations are quantitative. L. C. Hurd [53] shows that *rhenium* concentrates with arsenic in the Prescott–Johnson system [54] of analysis. He points out that sublimation methods for the detection of rhenium in minerals may fail, and recommends opening up by a fusion when the mineral is insoluble in hydrochloric or nitric acid. He adds that rhenium is probably best detected [55] by the thiocyanate reaction after molybdenum has been removed as a xanthic acid complex soluble in chloroform.

Antipyrine is chosen from a number of organic bases as the best reagent for *antimony*, with which it yields a yellowish-orange precipitate in the presence of potassium iodide; tin gives a white precipitate, but here the reaction is less sensitive. The reaction is applied after digestion of the arsenic, antimony, and tin sulphides of Group II*b* with hydrochloric acid.[56]

For the detection of *platinum* in small amount in minerals, alloys, and the like, the alkaline solution is treated with potassium iodide and acetic acid and a reddish-brown or rose colour appears if $Pt^{\cdot\cdot\cdot\cdot}$ is present. When precipitated from sodium tellurite by sulphur dioxide, tellurium separates platinum, gold, selenium, molybdenum, and mercury from other metals and so concentrates the platinum.[57]

The formation of red compounds with 4-methyl-1 : 2- and 4-chloro-1 : 2-dithiolbenzene (" dithiol ") is used as a test for *tin* by R. E. D. Clark.[58] These reagents, it is said, can be employed in the presence of all other metals when the colour of the mercaptides which they may form is not intense enough to mask the red colour due to tin, but

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[50] A. B. Levin, *Z. anal. Chem.*, 1936, **105**, 328; M. B. Schtschigol and N. M. Doubinski, *Ann. Chim. analyt.*, 1936, [iii], **18**, 257; V. J. Petraschenj, *Z. anal. Chem.*, 1936, **106**, 330.

[51] E. Chirnoagă, *ibid.*, 1936, **104**, 356.

[52] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 63; E. R. Caley, *J. Amer. Chem. Soc.*, 1932, **54**, 4112.

[53] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 11.

[54] R. K. McAlpine and B. A. Soule, "Qualitative Chemical Analysis," 1933.

[55] See L. C. Hurd and B. J. Babler, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 112, for determination of rhenium.

[56] J. A. Gautier, *J. Pharm. Chim.*, 1936, [viii], **23**, 283.

[57] S. K. Hagen, *Mikrochem.*, 1936, **20**, 180.

[58] *Analyst*, 1936, **61**, 242.

the only metals likely to interfere are copper, bismuth, and nickel. Unfortunately, like many reagents recommended for colour reactions, these thiolbenzenes are unstable and must be freshly prepared or stored in hydrogen. The test will undoubtedly be useful, but it seems that the ideal reagent for tin has yet to be found.[59]

The white precipitate which $\mathrm{Sn}^{\cdot\cdot\cdot\cdot}$ in hydrochloric or sulphuric acid forms with nitrophenylarsinic acid on boiling provides another selective test for this element which can be applied to its detection in alloys since the majority of metals likely to be present in such a case do not interfere. The material under investigation is first treated with concentrated nitric acid and the test made on the hydrochloric acid solution of the metastannic acid thus produced.[60]

In the absence of mercury, silver, and thallium, *copper* can be detected (and determined) in the presence of relatively large amounts of bismuth, cadmium, lead, and zinc by means of the yellow ammine $\mathrm{Cu[Cr(CNS)_4(NH_3)_2]}$, which is precipitated by the addition of Reinecke's salt to $\mathrm{Cu}^{\cdot\cdot}$ ions reduced to $\mathrm{Cu}^{\cdot}$ by $\mathrm{K_2SnCl_4,2H_2O}$ in hydrochloric acid solution,[61] and since cupric ions give no precipitate, the same reagent serves for the sensitive detection (and determination) of *mercury*, as $\mathrm{Hg[Cr(CNS)_4(NH_3)_2]_2}$, in the presence of many other metals.[62] After removal of copper by means of potassium thiocyanate, *cadmium* can be detected by 2 : 7-diaminofluorene, which is preferred to hydrogen sulphide for this purpose.[63]

In view of the utility of ammonium mercuric thiocyanate as a confirmatory test for *zinc*, determinations of the solubilities of zinc mercuric thiocyanate in alkali-salt solutions are of interest, as is the conclusion that zinc should be in the form of nitrate when this test is applied.[64]

According to H. Ditz and R. Hellebrand,[65] the sensitivity of the ammonium thiocyanate–acetone reaction for *cobalt* is much reduced if accompanying iron is removed either by sodium carbonate or by the formation of a complex fluoride. Removal by calcium carbonate, however, leaves the sensitivity unchanged and then 1·5 mg. of cobalt per litre can be detected in the presence of no less than 15 g. of iron. F. P. Dwyer[66] has also examined this reaction and finds that

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[59] *Ann. Reports*, 1935, **32**, 459; cf. also this Report, p. 462.

[60] B. Tougarinoff, *Bull. Soc. chim. Belg.*, 1936, **45**, 542.

[61] C. Mahr, *Z. anorg. Chem.*, 1935, **225**, 386.

[62] *Idem*, *Z. anal. Chem.*, 1936, **104**, 241.

[63] E. L. Niño and F. Calvert, *Anal. Fis. Quim.*, 1934, **32**, 698; cf. also A. W. Scott and E. G. Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 2541.

[64] B. V. J. Cuvelier and F. Bosch, *Natuurwetensch. Tijds.*, 1936, **18**, 9; see also B. V. J. Cuvelier, *Z. anal. Chem.*, 1935, **102**, 16.

[65] *Z. anorg. Chem.*, 1935, **225**, 73; see also *idem*, *ibid.*, 1934, **219**, 97.

[66] *J. Proc. Austral. Chem. Inst.*, 1936, **3**, 239.

the addition of ammonium acetate and tartaric acid to prevent interference from iron also leads to a serious loss of sensitivity, and he prefers to add potassium ammonium fluoride or, better still, sodium ammonium hydrogen phosphate, for this purpose.

In view of the peculiar behaviour of precipitated nickel and cobalt sulphides towards mineral acids, which is utilised in so many schemes of analysis and for which a satisfactory explanation has yet to be established, it is of interest to note that, according to A. M. Middleton and A. M. Ward,[67] the precipitates which are usually obtained in qualitative analysis are oxygenated and not the normal sulphides.

A mixture of potassium ferrocyanide and $Cu(NH_3)_4SO_4,H_2O$ is stated to give a sky-blue precipitate with *calcium* ions,[68] whilst new and more sensitive reagents described for *magnesium* [69] are *p*-nitrobenzenediazoamino-4-nitronaphthalene, *p*-nitrobenzenediazoaminobenzene, and 4-nitro-4′-amino-1 : 1′-azonaphthalene. It is claimed that no other metal hydroxide, even those of beryllium or the rare earths, gives a blue colour with the last reagent.

Several papers have been concerned with the removal of *phosphate* ions in qualitative analysis, and of these S. Ishimaru's contributions [70] are by far the most comprehensive. He finds that (i) PO_4''' can be completely removed from a solution just acid to methyl-orange by addition of ferric nitrate, and this is more convenient than the lead method which can be applied satisfactorily only after removal of Group III*a* and manganese, (ii) precipitation with $Bi^{\cdot\cdot\cdot}$ leads to less occlusion and adsorption of other ions by the precipitate than the iron method, but is less satisfactory in the presence of a high iron concentration, (iii) the zirconium method equals that of the iron in merit, (iv) precipitation with tin leads to loss of iron and chromium, but can be adopted after removal of the aluminium group and manganese, Reynoso's procedure [71] being the best, and (v) T. B. Smith's formate method [72] is the most suitable of all the methods advanced for elimination of the effects of phosphate ions based on the addition of excess of phosphate or oxalate. It is finally concluded that, in so far as accuracy is concerned, the bismuth method, except in the case of a high iron content, is the best of the many methods which have been examined in considerable detail in this series of investigations. L. J. Curtman and T. B. Greenslade [73] also find that with the tin and the ferric chloride method loss of cations is serious. Both these

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[67] *J.*, 1935, 1459.

[68] S. A. Celsi, *Anal. Farm. Bioquím.*, 1934, **5**, 85.

[69] F. P. Dwyer, *J. Proc. Austral. Chem. Inst.*, 1936, **3**, 184, 224.

[70] *Sci. Rep. Tôhoku*, 1935, **24**, 426, 439, 448, 461, 473.

[71] *Ann. Chim. Phys.*, 1852, **34**, 320.

[72] *J.*, 1933, 253.

[73] *J. Chem. Educ.*, 1936, **13**, 238.

and the zirconyl chloride method are all efficient in removing phosphate, but they consider that the last is the most rapid, effective, and convenient. C. N. Potschinok [74] eliminates this ion as aluminium phosphate, and S. Augusti [75] uses lead acetate in acetic acid solution to remove oxalate, fluoride, silicate, and silicofluoride ions as well. V. J. Petraschenj [76] has outlined a scheme for cations of the third and the fourth analytical group in the presence of phosphate, and W. Fischer, W. Dietz, K. Brünger, and H. Grieneisen [77] have investigated the same subject in considerable detail, putting forward new schemes for these groups. The sensitivity of the phosphomolybdate reaction is said to be enhanced by the addition of a suitably-prepared glycerol–gelatin solution.[78]

In order to detect very small percentages of non-metallic impurities in metals, the sample of metal is made the cathode in the electrolysis of dilute sulphuric acid or dilute sodium hydroxide plus potassium cyanide. Phosphorus, arsenic, antimony, sulphur, selenium, and tellurium, combined or in solid solution, are reduced to their hydrides, which are identified by filter-paper impregnated with suitable reagents; 0·001% of phosphorus, for example, can thus be detected.[79]

Small amounts of *bromide* in sodium chloride can be identified by a modification of the colour reaction with fuchsin,[80] and *bromates* are detected in the presence of potassium chlorate and bromide by a greenish-yellow colour which develops with fluorescein.[81] In 4N-hydrochloric acid solution, bromates rapidly decolorise methyl-orange, and this forms the basis of a test in the presence of other oxidising agents such as chlorates, iodates, nitrates, persulphates, dichromates, ferricyanides, and nitrites. The same reaction can also be used to detect small amounts of bromate in a large excess of chloride or bromide.[82]

Methods for dealing with insoluble *ferricyanides* and the detection of the ferricyanide ion with leuco-malachite green or benzidine are described by L. Kuhlberg.[83] According to J. Plank,[84] freshly-prepared ceric sulphate plus potassium carbonate will detect 1 part of *hydrogen peroxide* in 160,000 parts of solution.

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[74] *J. Appl. Chem. Russia*, 1936, **9**, 140.

[75] *Ann. Chim. appl.*, 1935, **25**, 448.

[76] *Z. anal. Chem.*, 1936, **106**, 241.

[77] *Angew. Chem.*, 1936, **49**, 719.

[78] A. Steigmann, *Chem.-Ztg.*, 1936, **60**, 129.

[79] K. W. Fröhlich, *Angew. Chem.*, 1935, **48**, 624.

[80] R. C. López, *Farm. moderna*, 1935, **46**, 55; see also F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1935, p. 278.

[81] F. L. Hahn, *Mikrochem.*, 1936, **20**, 236.

[82] I. M. Korenman, *Z. anal. Chem.*, 1935, **103**, 269.

[83] *Ibid.*, 1936, **106**, 30.

[84] *Magyar Chem. Fol.*, 1934, **40**, 105.

Drop Reactions.—The output this year of papers dealing with these tests, conveniently but unfortunately spoken of as " spot " tests, is somewhat less than in previous years, but the importance and interest of the subject make it desirable again [85] to summarise the work which has been done. The tendency too readily to regard these tests as specific still exists in some quarters, although the series of critical investigations which are being undertaken by certain workers may help to correct this erroneous view.* For example, having shown that the cacothelin test for tin is by no means specific,[86] J. B. Ficklen, I. L. Newell, and N. R. Pike [87] have turned their attention to the cinchonine–potassium iodide reagent for *bismuth*, which likewise is not truly specific, and to *p*-nitrobenzeneazoresorcinol for *magnesium*, which should be used only when ions of Groups I, II, and III, and ammonium have been removed.[88]

The use of drop reactions in the identification of substances soluble with difficulty in acids, such as the silver halides, insoluble sulphates and fluorides, ignited oxides, silica, etc., is described by F. Feigl,[89] and A. A. Benedetti-Pichler and W. F. Spikes have presented a scheme for the separation, identification, and estimation of mixtures of *thallium*, *lead*, and *silver* using 0·5—1 mg. of solid material.[90] This is the first of a series of papers on qualitative separations on the micro-scale, and those who, like the Reporter, hold the view that group separations are still essential for the analysis of any but the simplest materials, and that the future of qualitative analysis lies in the judicious combination of these separations and drop reactions, will look forward with considerable interest to the contributions

[85] Cf. *Ann. Reports*, 1935, **32**, 471.

[86] Cf. *ibid.*, p. 472, ref. (36).

[87] *Z. anal. Chem.*, 1936, **104**, 30.

[88] I. L. Newell, N. R. Pike, and J. B. Ficklen, *Z. anorg. Chem.*, 1935, **225**, 281.

[89] *Mikrochem.*, 1936, **20**, 198.

[90] *Ibid.*, 1936, **19**, 239.

* Part of the misapprehension which has arisen as to the true selectivity of organic reagents now employed in drop reactions may be due to a confusion of terms. Feigl, who has done so much to advance this branch of analysis—and, presumably, German-speaking authors have followed him—uses the term " specific " in a wider sense than is customary with English-speaking people, but he is careful both in his book (*op. cit.*, p. 10) and in his latest article [*Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 401] to differentiate between " specific " reagents and those he calls " special " reagents, few of which, as he points out, are known at the present time. " Special " reactions or " Sonderreaktionen " are, in the ideal case, limited solely to one substance and are not subject to interference by the presence of any other, and it is these " special " reactions and reagents which we regard as " specific," since with us this term implies a property characteristic of and peculiar to one substance alone.

which are to follow, based, as they are to be, on the thorough and exhaustive investigations of Noyes and his school.[91]

A new test for *silver* with what is probably ethyl 5-keto-2-thion-hexahydropyrimidine-4-carboxylate is said [92] to be more selective than, and about as sensitive as, the rhodanine base used by F. Feigl.[93] *Lead* can be detected in the presence of a large excess of barium, copper, iron, manganese, nickel, etc., by applying the triple nitrite test to the ammonium acetate solution of the precipitated sulphate,[94] and tervalent *thallium* can be recognised by the intense green colour which it gives with leuco-*o*-nitrodiamant green.[95] The action of *cupric* salts on benzidine has been discussed, and a reagent consisting of *o*-tolidine (which gives tolidine-blue) and ammonium thiocyanate in acetone is preferred [96] as a more sensitive test. After conversion of the iron into $[FeF_6]^{\cdots}$, it is claimed that 0·00016% of copper in iron salts can be detected. F. Feigl and R. Uzel [97] utilise as a drop reaction for *copper* the yellow to red colour,[98] due to tervalent copper, which is formed with potassium tellurate or periodate in alkaline solution and in the presence of an oxidising agent such as potassium persulphate. A reversal of the test serves to detect either *tellurium*, for which drop reactions are all too few, or *periodic acid* which can then be sought in the presence of other oxidising anions. Periodic acid, and tellurium in the presence of a very large excess of selenium, can both be identified [97] by their inhibiting action on the catalytic effect of copper in the oxidation of manganese to manganate ions by sodium hypobromite. Drop methods for *bismuth* have also been adapted from well-known macro-reactions.[1]

Induced precipitation is well known as a device for collecting traces of an element from a very dilute solution, and it is now employed for the detection of small quantities of *titanium* and *zirconium*.[2] Zirconium is added to the suspected titanium solution and precipitated by means of arsenic acid; coprecipitated titanium is confirmed in the usual way with hydrogen peroxide. In effect, the sensitivity of the hydrogen peroxide test thus becomes much increased. The procedure detailed is particularly useful when much iron, vanadium, etc., which interfere in the ordinary way

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[91] See A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," 1927.

[92] S. E. Sheppard and H. R. Brigham, *J. Amer. Chem. Soc.*, 1936, **58**, 1046.

[93] *Z. anal. Chem.*, 1928, **74**, 380.

[94] I. M. Korenman and S. S. Messonshnik, *Mikrochem.*, 1936, **20**, 189.

[95] L. Kuhlberg, *ibid.*, 1936, **19**, 183.

[96] *Idem, ibid.*, 1936, **20**, 153.

[97] *Ibid.*, 1936, **19**, 132.

[98] B. Brauner and B. Kuzma, *Ber.*, 1907, **40**, 3362.

[1] N. A. Tananaev and A. V. Tananaeva, *J. Appl. Chem. Russia*, 1935, **8**, 1457.

[2] F. Feigl and E. Rajmann, *Mikrochem.*, 1935, **19**, 60.

with this test, are present. By a reversal of the process, small amounts of zirconium can be gathered with titanium arsenate and confirmed with azoarsinic acid.

In addition to providing a serviceable test for aluminium, morin can also be used for *gallium*, but unlike the case of aluminium, the fluorescence which it gives is not suppressed when sodium fluoride is added.[3] In daylight the fluorescence of these two elements with morin appears to be specific, but in ultra-violet light other elements also fluoresce. This fluorescence with morin has served to detect gallium in minerals such as zinc blende and arsenopyrite.[3] Other colour reactions for gallium, *viz.*, a bright red lake with alizarin in presence of ammonia and ammonium chloride, and a reddish-brown coloration or precipitate with potassium ferrocyanide, manganese chloride and potassium bromate, applicable when aluminium and indium are present, have also been described and applied to minerals.[4]

Drop methods for *cerium* with leuco-malachite-green,[5] *beryllium* with alkannin and naphthazarin,[6] *cobalt* with $Na_2[Fe(CN)_5NO]$ and piperidine in acetic acid solution,[7] and *ammonium* with Nessler's reagent [8] have been worked out. The sensitivity of the benzidine-blue test for *dichromate* is increased by the addition of hydrogen peroxide, according to L. Kuhlberg,[9] who adds that greater sensitivity is attained when *o*-tolidine replaces benzidine. The formation of octahedral crystals of a triple nitrite with praseodymium nitrate and sodium nitrite provides a sensitive test for *cæsium* which is not affected by the presence of potassium or rubidium.[10]

The ferrous sulphate test for *hydroxylamine* has been put on a micro-basis by F. Feigl and R. Uzel,[11] the ammonia evolved being identified by its action on silver nitrate and manganese sulphate;[12] 0·1 γ of hydroxylamine, it is claimed, can thus be detected, and 0·5 γ in the presence of a 3000-fold excess of hydrazine.

A selection of the Behrens tests [13] considered to be the most satisfactory in the actual practice of determinative mineralogy,* is de-

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[3] G. Beck, *Mikrochem.*, 1936, **20**, 194.

[4] N. S. Poluektov, *ibid.*, 1936, **19**, 248.

[5] L. Kuhlberg, *J. Appl. Chem. Russia*, 1935, **8**, 1452.

[6] J. Dubský and E. Krametz, *Mikrochem.*, 1936, **20**, 57.

[7] F. Feigl and R. Uzel, *ibid.*, 1936, **19**, 132.

[8] N. A. Tananaev and A. A. Budkevitsch, *J. Appl. Chem. Russia*, 1936, **9**, 362.

[9] *Mikrochem.*, 1936, **20**, 244.

[10] H. C. Goswami and P. B. Sarkar, *J. Indian Chem. Soc.*, 1935, **12**, 608.

[11] *Mikrochem.*, 1936, **19**, 132.

[12] F. Feigl, *op. cit.*, p. 271.

[13] See *Ann. Reports*, 1935, **32**, 474.

* For the detection in rocks and minerals of molybdenum, lead, and cobalt by means of their colour reactions with calcium xanthate, benzidine, and alkali thiocyanates, respectively, see H. Leitmeier and F. Feigl, *Tsch. Min. Petr. Mitt.*, 1936, **47**, 313.

scribed and illustrated by L. W. Staples,[14] who has also given details[15] of a microchemical test for *silicon*.[16] This depends on the formation of sodium silicofluoride from silicon tetrafluoride and its recognition under the microscope, and is claimed to be better than the metaphosphate bead, the rubidium silicomolybdate, or the benzidine test.

Electro-capillary methods of drop analysis have also been discussed by various authors [17] during the past year.

In the drop reactions mentioned in this section, the limiting amount of an element or ion which can be detected is of the order of 10^{-6} g. or less, but attention must always be paid to the possible presence of other constituents which frequently necessitate a modified procedure with a resultant loss of sensitivity.

L. S. T.

QUANTITATIVE COLORIMETRIC ANALYSIS.

During the past few years publications relating to colorimetric methods of analysis have been so numerous that for the present Report it has been possible to refer only to a selection which conveniently illustrates the progress that has been made.

The essentials of colorimetric analysis are : (1) preparation of a solution of a suitable coloured derivative, (2) evaluation of this solution by measurement of its light absorptive power. It is desirable to consider (2) in some detail, since it is the factor common to all colorimetric analyses.

"Colour" Measurement or Comparison.—Measurements are essentially relative, ultimately in terms of similar solutions of the same substance in known concentration. For convenience, artificial standards are sometimes used, *e.g.*, Lovibond glasses, liquids such as ferric chloride solutions,[1] aqueous picric acid, and aqueous potassium chromate.[2] The disadvantage of this method is that the spectral absorption curves of the test solutions and the sub-standard glasses or solutions may be far from identical.[3] Errors due to this cause are

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[14] *Amer. Min.*, 1936, **21**, 613.

[15] *Ibid.*, p. 379.

[16] See W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1936, **61**, 454, concerning the inadequacy of certain tests for tungsten.

[17] S. I. Dijatschkovski, *J. Gen. Chem. Russia*, 1935, **5**, 728; A. F. Orlenko, *ibid.*, 1935, **5**, 1091; H. Fritz, *Mikrochem.*, 1935, **19**, 6.

[1] M. G. Mellon and C. T. Kasline, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 187; cf. also *ibid.*, 1936, **8**, 463.

[2] R. Strohecker, R. Vaubel, and K. Breitwieser, *Z. anal. Chem.*, 1935, **103**, 1.

[3] Cf. J. P. Mehlig and M. G. Mellon, *J. Physical Chem.*, 1931, **35**, 3397; A. L. Bacharach and E. Lester Smith, *Analyst*, 1934, **59**, 70.

greatly magnified in the case of observers suffering from partial colour-blindness.[4] Better results may be anticipated in the rare cases where it is possible to prepare a sub-standard which has absorption curves practically identical with those of the test solution.[5]

Instruments.

In the simplest form of measurement using comparison tubes of the Nessler-cylinder type, the probable error is rarely less than ± 3%, and in some cases may be as high as ± 8%. The accuracy obtainable with colorimeters of the Duboscq type is not much greater.[6]

It appears to be now generally recognised, however, that in an instrument using white light, Beer's law cannot apply rigidly, with the result that empirical correction curves are necessary.[7] Moreover, owing to the diluting effect of the white light, the sensitivity is less than that of spectrophotometric methods. The use of suitable coloured filters appreciably increases the accuracy of the Duboscq type of instrument.[8]

Measurement of Absorption Density.—In modern instruments, the relative absorption density of the coloured solution, for light of wavelength approximating to that for which the solution shows a maximum selective absorption, is measured. The obvious advantages are (1) maximum sensitivity, and (2) a rectilinear (logarithmic) calibration curve, in accordance with Beer's law. A further important advantage is that, once a calibration curve has been constructed, there is no necessity to prepare the colour standards each time an analysis is made.

Undoubtedly the best method of measuring the absorption density is by means of the spectrophotometer, whereby measurements may be made over a very narrow range (*ca.* 50 A.) at any desired wavelength in the visible spectrum. By measurement at two suitable wave-lengths, it is often possible to determine two coloured substances in admixture.[4] By use of the quartz spectrograph, measurement can be extended to the ultra-violet, opening up an important field, *e.g.*, the determination of vitamin A by measurement of the absorption density at 3280 A.

Possibly from considerations of cost, references to the employment

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[4] F. Twyman and G. F. Lothian, *Proc. Physical Soc.*, 1933, **45**, 643.

[5] H. W. Swank and M. G. Mellon, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 348; W. D. McFarlane, *ibid.*, 1936, **8**, 124.

[6] A. Thiel, *Ber.*, 1935, **68**, 1015; *Z. anal. Chem.*, 1936, **106**, 281.

[7] J. H. Yoe, "Photometric Chemical Analysis," Vol. 1, Colorimetry; cf. A. P. Mussakin, *Z. anal. Chem.*, 1936, **105**, 351.

[8] W. D. Armstrong, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 300; A. Thiel, *loc. cit.*, ref. (6); R. J. Robinson and H. E. Wirth, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 147.

of the spectrophotometer for colorimetric chemical analysis are relatively few, but it has undoubtedly proved of value in initial research on individual colorimetric methods for the determination of the full spectral absorption curve of the coloured solution. This is exemplified in the studies of H. W. Swank and M. G. Mellon [5] on colorimetric standards for silica, and in the determination of vitamin-*D*.[9]

In the Pulfrich step photometer, colour filters are employed; consequently, the absorption densities determined are for light of comparatively broad wave-length range, and have relative rather than absolute significance. As with the spectrophotometer, the instrument enables a permanent calibration curve to be constructed. As an alternative to the mechanical (variable shutter) photometric device of the Pulfrich, use is made of a neutral grey solution of variable thickness for reducing the intensity of the direct beam in the " absolute " colorimeter.[10]

Photo-electric Instruments.—These should be described as spectrophotometers or absorptiometers, rather than colorimeters. The photo-electric cells, which may be of the photo-emission or the semiconducting type, can be used (1) as a null-point instrument to replace the eye in a spectrophotometer with polarising photometer [11] or Duboscq colorimeter,[12] (2) to afford a direct measure of light intensity and hence of absorption density. Instruments in the second class may be divided into two groups depending upon the number of photo-cells employed.

(a) *One-cell type.* The solution to be measured is interposed between the cell and the source of light, and the absorption of light by the solution is measured directly by determining the current output of the photo-electric cell in relation to the value obtained with the pure solvent.[13] In instruments of this type it is of paramount importance to use a light source of constant intensity; this may be realised by incorporating a Barretter (current-regulating) lamp in a circuit " buffered " by an accumulator.[14] In the case of

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[9] H. Brockmann and Y. H. Chen, *Z. physiol. Chem.*, 1936, **241**, 129.

[10] A. Thiel, *Z. anal. Chem.*, 1933, **94**, 170; A. Thiel and W. Thiel, *Chem. Fabr.*, 1932, 409; A. Thiel, *ibid.*, 1934, **7**, 383.

[11] M. G. Mellon and C. T. Kasline, *loc. cit.*, ref. (1); A. G. Winn, *Trans. Faraday Soc.*, 1933, **29**, 689.

[12] G. Bernheim and G. Revillon, *Ann. Falsif.*, 1936, **29**, 5; cf. also A. Goudsmit and W. H. Summerson, *J. Biol. Chem.*, 1935, **111**, 421; E. W. H. Selwyn, *J. Sci. Instr.*, 1933, **10**, 116.

[13] J. H. Yoe and T. B. Crumpler, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 281; N. Strafford, *Analyst*, 1936, **61**, 170; R. S. W. Thorne and L. R. Bishop, *J. Inst. Brew.*, 1936, **42**, 15; L. E. Howlett, *Canadian J. Res.*, 1936, **14**, *A*, 38; R. A. Osborn, *J. Assoc. Off. Agric. Chem.*, 1934, **17**, 135.

[14] N. Strafford, *loc. cit.*, ref. (13).

cells showing a " fatigue " effect it is necessary to allow the photo-cell to attain its equilibrium current after each change of light intensity.[15]

(b) *Two-cell type.* Two photo-electric cells illuminated by the same source of light are balanced against each other through a galvanometer. The test solution is placed before one cell, the pure solvent before the other, and the current output difference measured directly.[16] Variations due to small fluctuations of the light source are automatically cancelled in an instrument of this type.

Photo-emission cells with different characteristic response curves are available, permitting the choice of one having maximum response to the coloured light under measurement.[17]

Coloured light in most instruments is obtained by filtering white light by colour filters, as in the Pulfrich photometer. More nearly monochromatic light is obtained by filtering the light from metal-vapour discharge lamps, *e.g.*, mercury or sodium.[18]

When a monochromator of the spectroscope type is used, the light is of such relatively low intensity that valve amplification of the photo-electric current is necessary.

Since most colour filters are comparatively transparent to infra-red rays, to which the photo-electric cells are responsive, an additional filter must be used (" minus-infra-red ") in order to obtain maximum absorption-density readings.[19] Weston Electrical Instrument Co. provide a " Viscor " filter which fulfils this purpose.[20]

Accuracy of Photometric Colorimetric Analysis.—Even with the best instruments, careful choice of operating conditions is necessary to ensure the highest accuracy. According to F. Twyman and G. F. Lothian,[21] the percentage error is at a minimum at an absorption density of between 1·5 and 2·0 in the case of a visual spectrophotometer, and of 0·43 in objective (photo-electric) instruments. These authors also consider that, although theoretically photo-electric methods give much greater sensitivity of discrimination than the eye, yet visual methods are more trustworthy as far as absolute measurements are concerned. In the Reporter's opinion, a simple and

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[15] J. H. Yoe and T. B. Crumpler, *loc. cit.*, ref. (13); N. Strafford, *loc. cit.*, ref. (13).

[16] C. Zinzadze, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 280; R. B. Withrow, C. L. Shrewsbury, and H. R. Kraybill, *ibid.*, 1936, **8**, 214; B. Lange, *Chem. Fabr.*, 1934, **7**, 45.

[17] R. B. Withrow, C. L. Shrewsbury, and H. R. Kraybill, *loc. cit.*, ref. (16).

[18] R. Sewig and F. Müller, *Chem. Fabr.*, 1934, **7**, 25; H. Alterthum and M. Reger, *ibid.*, 1933, **6**, 283.

[19] E. R. Bolton and K. A. Williams, *Analyst*, 1935, **60**, 447; N. Strafford, *loc. cit.*, ref. (13); cf. also R. Fonteyne and P. de Smet, *Mikrochem.*, 1933, **13**, 289.

[20] *J. Sci. Instr.*, 1936, **13**, 338.

[21] *Loc. cit.*, ref. (4).

relatively inexpensive photo-electric instrument,[22] properly used, is as accurate as a spectrophotometer for the relative measurements required by colorimetric analysis.

Nephelometry.

There is no sharp division between colorimetry and nephelometry. Some of the organometallic derivatives, such as copper diethyldithiocarbamate in aqueous media, and sulphides such as lead sulphide may be described as being in colloidal " solution " in colorimetric tests. Particular care in preparation of the standard and test solutions is necessary in order to obtain reproducible results and compliance with Beer's law. The use of protective colloids is of value in this connection.[23]

Photo-electric measurements have shown that transmission of light by two similarly prepared colloidal lead sulphide " solutions " apparently equal in shade to the eye may be appreciably different.[24] For true nephelometric determinations, *e.g.*, of zinc as ferrocyanide, the photo-electric absorptiometer affords an appreciably greater accuracy than visual comparison.[25] K. W. Franke, R. Burris, and R. S. Hutton [26] describe a novel procedure by which coloured precipitates of colloidal fineness, *e.g.*, selenium, are filtered on to a mat of barium sulphate. Permanent colour standards are thus prepared.

Colorimetric Determination of the Elements.

Although so far almost exclusively used for determination of minor amounts of an element, in the Reporter's opinion there are adequate reasons (mainly saving of time) why much wider use should be made of colorimetric methods for determination of elements present as major constituents.* At the same time, the opinion is recorded that, for micro-analysis, colorimetric methods are at least as accurate as, and usually simpler and more convenient than, alternative methods; in many cases, moreover, alternative methods of adequate sensitivity do not exist.

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[22] Cf. N. Strafford, *loc. cit.*, ref. (13).

[23] L. de Brouckère and S. Solowiejczyk, *Bull. Soc. chim. Belg.*, 1934, **43**, 597; C. Zinzadze, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 227.

[24] Second Report of the Sub-Committee on the Determination of Arsenic, Lead and other Poisonous Metals in Food Colouring Materials to the Analytical Methods Committee of the Society of Public Analysts : II, The Determination of Lead; *Analyst*, 1935, **60**, 541.

[25] N. Strafford, *loc. cit.*, ref. (13).

[26] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 435.

* As an example, J. P. Mehlig [*Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 387] claims that the copper content of ores (up to 22%) may be determined with a photo-electric spectrophotometer to an accuracy of ± 0·1%.

The first task of the analyst is to devise conditions ensuring specificity, and in spite of the availability of numerous organic reagents, cases in technical analysis where a preliminary separation is not necessary are the exception rather than the rule. The most important advance in recent years is in the application of organic reagents in organic solvents for separation of interfering elements, as well as for the formation of a coloured derivative. The following will serve as examples of modern technique in the inorganic field.

Lead.—A general method for the determination of lead in the presence of other metals involves isolation of the lead, first as sulphide and then as sulphate, followed by the application of the colloidal sulphide method, the limitations of which are discussed.[24]

The use of dithizone is recommended both for the separation of lead from most other metals,[27] and from bismuth,[28] and also for the actual colorimetric measurement. The latter may be applied to the red lead dithizone complex [29] or to the regenerated green dithizone.[30]

P. A. Clifford and H. J. Wichmann [31] show, from considerations of distribution between aqueous and organic media, that both these methods fail to give complete recovery of the lead, and they recommend a "mixed colour" photometric method in which complete extraction of lead is ensured by use of an excess of dithizone applied to a solution of optimum p_H value (9·0). They also criticise the methods for removal of bismuth referred to above, and suggest methods for preventing interference from tin.

It is of particular importance to employ a purified reagent free from oxidation products,[30] and to avoid the presence of oxidising reagents.[32]

In certain cases, the extraction of lead from aqueous solutions containing insoluble matter by means of a solution of dithizone is not complete owing to occlusion of lead by the insoluble matter.[24] Dithizone is, however, used for extracting insoluble lead compounds from spray residues.[33]

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[27] N. L. Allport and G. H. Skrimshire, *Analyst*, 1932, **57**, 440; *Pharm. J.*, 1932, **129**, 248; G. Roche Lynch, R. H. Slater, and T. G. Osler, *Analyst*, 1934, **59**, 787.

[28] S. L. Tompsett, *ibid.*, 1936, **61**, 591; C. E. Willoughby, E. S. Wilkins, jun., and E. O. Kraemer, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 285.

[29] J. R. Ross and C. C. Lucas, *J. Biol. Chem.*, 1935, **111**, 285; O. B. Winter, H. M. Robinson, F. W. Lamb, and E. J. Miller, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 265.

[30] H. Fischer and G. Leopoldi, *Angew. Chem.*, 1934, **47**, 90; F. Morton, *Analyst*, 1936, **61**, 465.

[31] *J. Assoc. Off. Agric. Chem.*, 1936, **19**, 130.

[32] S. L. Tompsett, *loc. cit.*, ref. (28).

[33] W. E. White, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 231.

Mercury.—For the determination of mercury, N. Strafford and P. F. Wyatt[34] recommend the reaction with *p*-dimethylaminobenzylidenerhodanine, which is less subject to interference than that with diphenylcarbazide or diphenylcarbazone. Preliminary separation of the mercury from most other metals is essential. H. Fischer and G. Leopoldi[35] and W. O. Winkler[36] separate and determine mercury as the dithizone complex.

Tin.—Since previous methods for tin depend merely on the reducing action of stannous salts, the appearance of a reagent which forms a coloured derivative with tin is welcome.[37] It must be noted, however, from the author's own findings, that the reaction is *not* specific for tin (see p. 449), a number of other metals, particularly copper, bismuth, and nickel, giving coloured derivatives.

Zinc.—W. Deckert[38] determines zinc, after removal of copper as sulphide, as the coloured complex obtained with dithizone in alkaline solution. Dithizone is also recommended by H. Fischer and G. Leopoldi.[39] A novel method for zinc consists in precipitating the metal, again after a preliminary separation and removal of copper as sulphide, as its complex with 8-hydroxyquinoline. The absorption density of the 8-hydroxyquinoline is then determined, after decomposition of the complex, in ultra-violet light.[40]

Copper.—Numerous papers continue to appear, most of them describing variations of well-known methods. C. A. Goethals[41] discusses the sensitivity of several colour reactions. General opinion seems to favour the dithiocarbamate method,[42] although it is recognised that preliminary separation of other metals is often necessary.[43] G. Bertrand and L. de Saint Rat[44] recommend urobilin as a selective reagent. H. Fischer and G. Leopoldi[45] determine copper as the dithizone complex in an organic solvent. E. Stolze[46] points out

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[34] *Analyst*, 1936, **61**, 528.

[35] *Z. anal. Chem.*, 1935, **103**, 241.

[36] *J. Assoc. Off. Agric. Chem.*, 1935, **18**, 638.

[37] R. E. D. Clark, *Analyst*, 1936, **61**, 242.

[38] *Z. anal. Chem.*, 1935, **100**, 385.

[39] *Ibid.*, 1936, **107**, 241.

[40] J. Dąbrowski and L. Marchlewski, *Biochem. Z.*, 1935, **282**, 387.

[41] *Z. anal. Chem.*, 1936, **104**, 170.

[42] T. Callan and J. A. R. Henderson, *Analyst*, 1929, **54**, 650.

[43] L. W. Conn, A. H. Johnson, H. A. Trebler, and V. Karpenko, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 15; N. D. Sylvester and L. H. Lampitt, *Analyst*, 1935, **60**, 376; E. Lasausse and L. Frocain, *J. Pharm. Chim.*, 1936, [viii], **23**, 77; B. Eisler, K. G. Rosdahl, and H. Theorell, *Biochem. Z.*, 1936, **285**, 76.

[44] *Compt. rend.*, 1936, **203**, 140.

[45] *Angew. Chem.*, 1934, **47**, 90.

[46] *Bodenk. Pflanzenernähr.*, 1936, **1**, 115.

that it is necessary to reduce any ferric salts before applying this method. N. Strafford [47] suggests the use of salicylaldoxime as a sensitive and specific nephelometric reagent.

Iron.—Attention continues to be paid to improvement of the thiocyanate [48] and the sulphosalicylic acid [49] method. [Incidentally, calcium (as oxalate) may be determined by its bleaching action on the iron–sulphosalicylic acid colour.][50] $\alpha\alpha'$-Dipyridyl is recommended as a colorimetric reagent.[51]

Aluminium.—Calcium salts and other interfering substances cause fictitiously high values in determinations with alizarin.[52] Interference from iron is prevented by its removal as thiocyanate in amyl alcohol.[53]

Germanium.—N. S. Poluektof [54] describes the determination of small quantities of germanium, the method depending on the blue colour formed by the reduction of germanomolybdic acid.

Titanium.—Titanium is determined by hydrogen peroxide [55] or by salicylic acid.[56]

Alkali Metals.—Existing methods for the colorimetric determination of potassium, involving the precipitation as cobaltinitrite, are reviewed, and a modified procedure is described by R. J. Robinson and G. L. Putnam.[57]

Sodium is determined as an aqueous yellow solution of its triple acetate with uranium and magnesium.[58]

Phosphorus and Silicon.—Considerable attention has been given

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[47] "The Detection and Determination of Small Amounts of Inorganic Substances by Colorimetric Methods," Institute of Chemistry Publication, 1933, p. 27; cf. also F. Alten, B. Wandrowsky, and E. Knippenberg, *Mikrochem.*, 1936, **20**, 77.

[48] K. Steinhauser and H. Ginsberg, *Z. anal. Chem.*, 1936, **104**, 385; G. E. Farrer, jun., *J. Biol. Chem.*, 1935, **110**, 685.

[49] F. Alten, H. Weiland, and E. Hille, *Z. anorg. Chem.*, 1933, **215**, 81; A. Thiel and O. Peter, *Z. anal. Chem.*, 1935, **103**, 161.

[50] L. Jendrassik and F. Takács, *Biochem. Z.*, 1934, **274**, 200.

[51] G. Bode, *Woch. Brau.*, 1933, **50**, 321; L. L. Engel, *J. Dent. Res.*, 1934, **14**, 273: W. D. McFarlane, *loc. cit.*, ref. (5); F. B. Shorland and E. M. Wall, *Biochem. J.*, 1936, **30**, 1049; H. I. Coombs, *ibid.*, p. 1588.

[52] D. F. Eveleth and V. V. Myers, *J. Biol. Chem.*, 1936, **113**, 449.

[53] A. P. Mussakin, *J. Appl. Chem. Russia*, 1936, **9**, 1340.

[54] *Z. anal. Chem.*, 1936, **105**, 23.

[55] H. Ginsberg, *Z. anorg. Chem.*, 1933, **211**, 401; 1935, **226**, 57; G. P. Lutschinski and A. I. Lichatscheva, *Z. anal. Chem.*, 1935, **103**, 196; H. A. Liebhafsky, *ibid.*, **105**, 113; L. Maillard and J. Ettori, *Compt. rend.*, 1936, **202**, 594.

[56] M. Schenk, *Helv. Chim. Acta*, 1936, **19**, 1127.

[57] *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 211.

[58] A. Elias, *Anal. Asoc. Quím. Argentina*, 1935, **23**, 1.

to the important determinations of phosphorus [59] and of silicon [60] by the molybdenum-blue reaction.

Determination of p_H *Value.*

According to E. A. Guggenheim and T. D. Schindler,[61] results of colorimetric p_H determinations by means of a Gillespie comparator are reproducible within 1%. M. Kilpatrick, E. F. Chase, and L. C. Riesch [62] maintain that the experimental error of the colorimeter method is about 5%, and of the electrometric method about 2·5%. A. G. de Almeida [63] plots dominant hue, expressed as a wave-length, against p_H for a series of indicators, and claims that it is possible to determine the p_H of an unknown solution more accurately than by electrometric methods.

Textile assistants such as sulphonated oils, sulphated and sulphonated fatty alcohols, sodium alkylnaphthalenesulphonates, etc., exert a specific effect on most indicators which is frequently a source of considerable error, even up to 1·0 unit, in the colorimetric determination of p_H.[64] This is discussed elsewhere in these Reports (p. 110).

Photometric Titrations.

Photometric methods may be employed for the accurate objective determination of the end-point in a colorimetric or turbidimetric titration. E. T. Bartholomew and E. C. Raby [65] determine alkali cyanides by titration with silver nitrate to the incipient development of turbidity, detected by a system of balanced photo-electric cells. S. Hirano [66] titrates mercuric chloride or nitrate with 0·01 or 0·001*N*-sodium sulphide in presence of gum-arabic as protective colloid, the end-point being indicated when the turbidity reaches a maximum value. In a similar manner he determines silver by titration with sodium chloride, in presence of starch.[67] He also describes methods for determining soluble sulphides,[68] gold,[69] and halides.[70]

[59] K. C. Scheel, *Z. anal. Chem.*, 1936, **105**, 256; R. Ammon and K. Hinsberg, *Z. physiol. Chem.*, 1936, **239**, 207; C. Zinzadze, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 227; K. Boratyński, *Z. anal. Chem.*, 1935, **102**, 421; H. Etienne, *Bull. Soc. chim. Belg.*, 1936, **45**, 516; H. L. Brose and E. B. Jones, *Nature*, 1936, **138**, 644.

[60] F. De Eds and C. W. Eddy, *J. Biol. Chem.*, 1936, **114**, 667; R. Strohecker, R. Vaubel, and R. Breitwieser, *Z. anal. Chem.*, 1935, **103**, 1.

[61] *J. Physical Chem.*, 1934, **38**, 543.

[62] *J. Amer. Chem. Soc.*, 1934, **56**, 2051.

[63] Diss., Lisbon, 1935.

[64] J. E. Smith and H. L. Jones, *J. Physical Chem.*, 1934, **38**, 243; H. L. Jones and J. E. Smith, *Amer. Dyestuff Rep.*, 1934, **23**, 423.

[65] *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 68.

[66] *J. Soc. Chem. Ind. Japan*, 1935, **38**, 646.

[67] *Ibid.*, 1934, **37**, 754B.

[68] *Ibid.*, 1935, **38**, 598B.

[69] *Ibid.*, 1934, **37**, 178B, 561B.

[70] *Ibid.*, p. 177B; 1935, **38**, 175.

F. Müller reviews the use of photo-electric cells in automatic titrations.[71]

Colorimetric Oxidation–reduction Reactions.—H. P. Lundgren [72] describes a modified Duboscq colorimeter used for following fading curves in oxidation–reduction reactions.

N. S.

ORGANIC ANALYSIS.

Elements.—Difficulties experienced in the determination of sulphur, oxygen, and nitrogen by the ter Meulen method [1] have now been overcome,[2] and it is claimed that satisfactory results for the estimation of nitrogen in compounds of high halogen content are obtained if soda–lime is placed both in front of and behind the catalyst.[3] Ultimate analysis of an organic substance may be based on pressure measurements after combustion in a bomb calorimeter.[4] Sulphur may also be satisfactorily determined by the bomb method,[5] and chlorine may be determined accurately by the rapid lamp method.[6] Convenient wet oxidation methods have been described for the determination of (*a*) sulphur and copper,[7] and (*b*) carbon and nitrogen.[8]

Qualitative.—When treated with nascent chlorine, *i.e.*, potassium permanganate in dilute hydrochloric acid, ketoximes give a bluish-green coloration, whilst aldoximes yield a solution which gives a red colour with ferric chloride : [9] certain aromatic aldoximes do not give this reaction. The reaction with hydroxylamine hydrochloride has been the basis of a somewhat elaborate scheme for the recognition of aldehydes, ketones, acids, acid chlorides, anhydrides, amides, esters, and lactones.[10]

The following reagents have been investigated for the identification of aldehydes and ketones : *p*-bromo-,[11] *m*-chloro-,[12] and *m*-

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[71] *Z. Elektrochem.*, 1934, **40**, 46.

[72] *Science*, 1934, **80**, 209.

[1] J. Gauthier, *Bull. Soc. chim.*, 1935, [v], **2**, 506.

[2] H. ter Meulen, *ibid.*, p. 1692.

[3] H. ter Meulen and H. J. Ravenswaay, *Chem. Weekblad*, 1936, **33**, 248.

[4] P. J. Merkus and A. H. White, *Proc. Amer. Gas Assoc.*, 1934, 991.

[5] H. C. Chiang and C. L. Tseng, *Sci. Rep. Nat. Univ. Peking*, 1936, **1**, 19.

[6] W. N. Malisoff, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 428.

[7] N. N. Melnikov, *J. Gen. Chem. Russia*, 1935, **5**, 839.

[8] C. N. Acharya, *Biochem. J.*, 1936, **30**, 241.

[9] E. Graf, *Anal. Fis. Quim.*, 1936, **34**, 91.

[10] *Idem*, *ibid.*, p. 95.

[11] S. M. Wang, Cheng-Heng Kao, Chung-Hsi Kao, and P. P. T. Sah, *Sci. Rep. Nat. Tsing Hua Univ.*, 1935, *A*, **3**, 279.

[12] P. P. T. Sah and C. S. Wu, *ibid.*, 1936, **3**, 443.

bromo-benzhydrazide,[13] *m*-tolylhydrazine,[14] which in conjunction with the *o*- and *p*-isomerides is suggested as a reagent for the identification of sugars,[15] β-naphthoylhydrazide,[16] and *m*-tolylsemicarbazide.[17] It has been shown that the melting points of many of the recorded 2 : 4-dinitrophenylhydrazones are incorrect; the use of *iso*propyl instead of ethyl alcohol in Brady's method gives purer compounds.[18]

3-Nitrobenzazide,[19] *p*-bromobenzazide,[20] and *m*-nitrobenzoylthiocarbimide [21] have been investigated as reagents for the identification of amines, and benzylamine and α-phenylethylamine salts [22] and 1-chloro-2 : 4-dinitrobenzene [23] are recommended for use in the identification of acids and phenols respectively.

Japanese acid clay is a powerful adsorbent for diamino-acids obtained in the hydrolysis of proteins, arginine being adsorbed to the extent of 86·8% compared with 8·45% for glycine.[24] A process is described for the removal of the adsorbed amino-acids and for the regeneration of the clay.[25]

It has been found that most ethers form peroxides on storage and tend to explode on dry distillation, and the use of certain reagents as peroxide destroyers and oxidation inhibitors has been investigated.[26] Phenolic ethers may be identified through their picrates, although some of the compounds are unstable in air.[27]

A simplified copper solution for use in sugar analysis is made up of 100 c.c. of 29·9% sodium hydroxide solution, 1 g. of copper sulphate, and 10 c.c. of water.[28]

Quantitative.—Accurate determination of the hydroxyl groups may be rapidly effected by heating the substance with pyridine–

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[13] Chung-Hsi Kao, T. Tao, Cheng-Heng Kao, and P. P. T. Sah, *J. Chinese Chem. Soc.*, 1936, **4**, 69.

[14] P. P. T. Sah and C. Z. Tseu, *Sci. Rep. Nat. Tsing Hua Univ.*, 1936, *A*, **3**, 403.

[15] *Idem, ibid.*, p. 409.

[16] H. Chen and P. P. T. Sah, *J. Chinese Chem. Soc.*, 1936, **4**, 62.

[17] P. P. T. Sah, S. M. Wang, and C. H. Kao, *ibid.*, p. 187.

[18] N. R. Campbell, *Analyst*, 1936, **61**, 391.

[19] K. Meng and P. P. T. Sah, *J. Chinese Chem. Soc.*, 1936, **4**, 75.

[20] P. P. T. Sah, C. H. Kao, and S. M. Wang, *ibid.*, p. 193.

[21] W. L. Tung, Cheng-Heng Kao, Chung-Hsi Kao, and P. P. T. Sah, *Sci. Rep. Nat. Tsing Hua Univ.*, 1935, *A*, **3**, 285.

[22] C. A. Buehler, L. Carson, and R. Edds, *J. Amer. Chem. Soc.*, 1935, **57**, 2181.

[23] R. W. Bost and F. Nicholson, *ibid.*, p. 2368.

[24] M. Mashino and N. Shikazono, *J. Soc. Chem. Ind. Japan*, 1936, **39**, 54B, 88B.

[25] *Idem, ibid.*, p. 136B.

[26] E. C. Williams, *Chem. and Ind.*, 1936, 580.

[27] O. L. Baril and G. A. Megrdichian, *J. Amer. Chem. Soc.*, 1936, **58**, 1415.

[28] E. J. Mueller, *J. Pharm. Chim.*, 1936, [viii], **24**, 18.

acetic anhydride, decomposing the product with water, and titrating the excess acetic acid.[29] The method is not valid with *tert.*-alcohols and gives low results with sugar alcohols. Small quantities of ethyl alcohol may be determined by an oxidation method.[30]

Reducing sugars may be determined by direct potassium ferricyanide titration,[31] or by back titration with ceric sulphate.[32] Quantitative differentiation of fructose and mannose in glucose–fructose–mannose mixtures is possible by the use of micro-organisms,[33] and sucrose inversions may be followed by means of the glass but not the quinhydrone electrode.[34] Accuracy is claimed for methods of determining the acetyl [35] and the nitrate [36] group in carbohydrate derivatives.

Errors in the titration of the amino-groups in amino-acids, etc., are minimised if glacial acetic acid is used as the solvent.[37]

Convenient methods are described for the determination of: toluidines in aqueous solution,[38] xylidine isomerides,[39] camphor by the titration of the hydrogen chloride liberated from hydroxylamine hydrochloride after oxime formation,[40] phenol and cresols in the presence of each other,[41] and pyridine in the presence of nicotine.[42]

The methods available for the titration of alkaloids in anhydrous media have been critically reviewed.[43]

Colorimetry.—Carbamide, urethanes, and carbazides give a cerise coloration on heating with vanillin in concentrated hydrochloric acid after pre-heating with phenylhydrazine hydrochloride.[44] Colour reactions are described for certain *o*-nitro-compounds,[45] *cyclo*pentadiene,[46] and tartaric, citric, and aconitic acids.[47]

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[29] M. Freed and A. M. Wynne, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 278.

[30] T. E. Friedemann and R. Klass, *J. Biol. Chem.*, 1936, **115**, 47.

[31] G. I. Solomos, *Bull. Soc. Chim. biol.*, 1935, **17**, 1465.

[32] W. Z. Hassid, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 138.

[33] T. F. Nicholson, *Biochem. J.*, 1936, **30**, 1804.

[34] H. P. Cady and J. D. Ingle, *J. Physical Chem.*, 1936, **40**, 837.

[35] A. Friedrich and H. Sternberg, *Biochem. Z.*, 1936, **286**, 20.

[36] J. Dewar and G. W. Brough, *J. Soc. Chem. Ind.*, 1936, **55**, 207.

[37] L. J. Harris, *Biochem. J.*, 1935, **29**, 2820; G. F. Nadeau and L. E. Branchen, *J. Amer. Chem. Soc.*, 1935, **57**, 1363.

[38] D. Cismaru, *Bul. Soc. Chim. România*, 1934, **16**, *A*, 37.

[39] B. P. Fedorov and A. A. Spriskov, *Z. anal. Chem.*, 1936, **105**, 412.

[40] R. Vandoni and G. Desseigne, *Bull. Soc. chim.*, 1935, [v], **2**, 1685.

[41] V. Miklaschevskaja, *Chim. Tverd. Topl.*, 1934, **5**, 553.

[42] R. L. Fratkin, L. P. Juravleva, and A. G. Blankschtein, *Sborn. Robot Chim. Otdela*, 1935, 88.

[43] G. N. Thomis, *J. Pharm. Chim.*, 1936, [viii], **24**, 162.

[44] J. A. Sanchez, *Ann. Chim. analyt.*, 1936, [iii], **18**, 65.

[45] P. K. Bose and S. Ram, *J. Indian Chem. Soc.*, 1935, **12**, 687.

[46] B. N. Afanasiev, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 15.

[47] R. Casares, *Anal. Fis. Quím.*, 1936, **34**, 594; O. Fürth and H. Herrmann, *Biochem. Z.*, 1935, **280**, 448.

The colours formed in the bromide–resorcinol reaction are traced to the intermediate formation of glyoxylic acid, and a solution of this acid is recommended as a reagent for the characterisation of phenols, phenolic acids, and the chief opium alkaloids.[48]

Spot tests are described for the detection of phenol,[49] oxalic acid,[50] and of benzidine and tolidine in the presence of each other.[51]

Micro-methods.—Methods for the determination of various organic groups have been reviewed,[52] and the technique detailed for the determination of carbon, hydrogen, nitrogen, halogen, and methoxyl as applied to samples of 0·001—0·01 g.[53]

The necessary data are given for the characterisation, by the examination of crystals under the microscope, of: alkaloids as picrates,[54] *d*- and *l*-cocaine after treatment with potassium permanganate,[55] and amino-acids as their phosphotungstates, phosphomolybdates, picrates, and flavianates.[56] Berberine gives characteristic micro-crystalline precipitates with a number of compounds of pharmacological importance.[57]

Accurate methods are described for the determination of: acetyl groups,[58] acetone,[59] oxalic acid, the permanganate titration in hot solution being shown to be untrustworthy,[60] glucose by the ferricyanide–ceric sulphate method,[61] and protein nitrogen in the presence of ammonium salts.[62]

Apparatus.—Improved apparatus is described for the microhydrogenation of organic compounds,[63] and for avoiding loss by spurting during ashing with nitric acid.[64]

An electrically-heated melting-point apparatus gives an accuracy of 0·5°,[65] and a method for the determination of setting points enables metastable forms fusing within 1° of each other to be de-

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[48] M. Pesez, *Bull. Soc. chim.*, 1936, [v], **3**, 676.

[49] Y. Kondo, *Mikrochem.*, 1936, **19**, 214.

[50] F. Feigl and O. Frehden, *ibid.*, 1935, **18**, 272.

[51] L. Kulberg, *J. Gen. Chem. Russia*, 1935, **5**, 1754.

[52] A. Lacourt, *Bull. Soc. chim. Belg.*, 1936, **45**, 313.

[53] C. Weygand and H. Hennig, *Chem. Fabr.*, 1936, **9**, 8.

[54] A. Ionesco-Matiu and E. Iliesco, *J. Pharm. Chim.*, 1936, [viii], **23**, 117.

[55] R. Cecconi, *Ann. Chim. appl.*, 1936, **26**, 218.

[56] B. Bullock and P. L. Kirk, *Mikrochem.*, 1935, **18**, 129; B. L. Crosby and P. L. Kirk, *ibid.*, p. 137.

[57] C. van Zijp, *Pharm. Weekblad*, 1936, **73**, 764.

[58] A. Elek and R. A. Harte, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 267.

[59] A. Lindenberg, *Compt. rend. Soc. Biol.*, 1936, **122**, 317.

[60] J. Renaudin, *J. Pharm. Chim.*, 1936, [viii], **23**, 447.

[61] R. Vanossi and R. Ferramola, *Anal. Asoc. Quim. Argentina*, 1935, **23**, 162.

[62] A. Roche and F. Marquet, *Bull. Soc. Chim. biol.*, 1935, **17**, 1630.

[63] H. Jackson and R. N. Jones, *J.*, 1936, 895.

[64] H. Kaunitz, *Mikrochem.*, 1936, **20**, 104.

[65] E. Dowzard and M. J. Russo, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 74.

tected.[66] A differential mercury manometer [67] is used for measuring boiling points with only a few drops of liquid.

Modern resistance glass enables simple all-glass water stills to be constructed, which compare favourably with metal stills for efficiency.[68] R. W. W.

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[66] F. Francis and F. J. E. Collins, *J.*, 1936, 137.

[67] R. Dolique, *Bull. Soc. chim.*, 1935, [v], **2**, 1832.

[68] B. Siede, *Chem.-Ztg.*, 1935, **59**, 925.

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