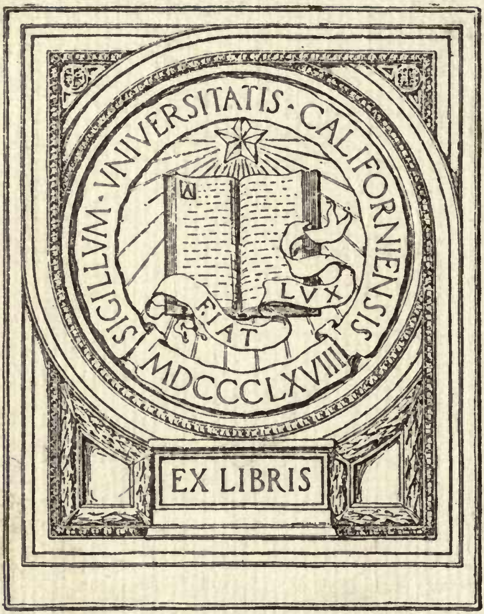

CATALYSIS IN THEORY AND PRACTICE

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CATALYSIS
IN THEORY AND PRACTICE

BY

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Πάντα ῥεῖ κοὐδὲν ἐν ταὐτῷ μένει

Panta rei kouden en tauto menei.

PREFACE

In the development of chemical science during the preceding hundred years, the steady progress in importance which catalytic operations have achieved is distinctly remarkable. Their importance emerges alike in the purely theoretical and in the technical aspects of the subject. In the natural order, also, investigation has shown how predominating a part the catalytic phenomenon plays. From the strictly utilitarian point of view, Industry was not slow to appreciate the advantages to be derived from the employment of agencies which should facilitate and "speed-up" manufacturing processes, nor was there lacking a body of scientific workers who steadily supplied the investigative and theoretical bases upon which such applications could be reared. As the scientific viewpoint developed the physiologist and biologist rapidly associated the simpler chemical phenomena with the more complex processes operating in living matter. To-day, therefore, catalysis intrudes prominently into all branches of natural science, both pure and applied.

The need for an exposition of the fundamental principles involved in this particular field of general chemistry and of the applicability of such principles in modern life has been widely felt and has offered to the authors the necessary inducement to prepare the present volume. An excellent chapter in Mellor's "Chemical Statics and Dynamics" has formed, hitherto, the sole treatment in English of the theoretical aspects of the problem. From time to time various papers have catalogued the more important practical applications of catalysis. The monograph of Sabatier, "La Catalyse en Chimie Organique," deals more particularly with the applications to preparative organic chemistry with slight reference to the physico-chemical theories involved. Dr. Gertrud Woker has compiled a detailed survey of the theoretical aspects of catalysis and of their application to the problems of analytical procedure, in Margosches's *Sammlung*, entitled, "Die Chemische Analyse," Vols. XI, XXI and XXIII. The volume entitled "Untersuchungen im Gebiete der Kinetik der Chemischen Reactionen und Katalyse," by the Russian, Orloff, and "La Catalisis Quimica," by P. E. Vittoria, are supplementary to the above volumes. From all these sources, to which we wish to acknowledge our indebtedness, we have freely drawn in an effort to obtain a systematic and comprehensive treatment of the whole subject.

For personal assistance in the compilation of the work we wish to express our thanks to Professor F. G. Donnan, F.R.S., for advice and for stimulating and continuous encouragement, and to Professor W. M. Bayliss, F.R.S., for a kindly criticism of the chapter dealing with Ferments and Enzyme Action.

The diagrams have been drawn by our laboratory assistant, Mr. A. Hiscocks, to whom we express our acknowledgments and thanks.

With a subject the literature of which is already so considerable and is increasing so rapidly and continuously, it is not possible to give an exhaustive summary of the scientific and technical references. The aim, rather, has been to embody in the text the main lines of development, choosing from the available examples suitable data for the purposes of illustration. It is hoped that such an object has been achieved. Criticism or additional information relative to the subjects treated will be welcomed.

The subject matter of the volume deals with the influence of catalysts in the reactivities of atoms and molecules among themselves. In the future, the problems of chemistry will centre more and more around the intra-atomic reactions and atomic structure. Already, the evidence is available that the atoms undergo processes of radio-active disintegration at definite but, thus far, unalterable speeds. Will the catalytic agencies be found which shall accelerate the velocity of atomic decay and render available the enormous stores of intra-atomic energy? Such is a fitting problem for the years that lie ahead.

LONDON, *November* 11*th*, 1918.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
Abh. Akad. Wiss. Berlin	Abhandlungen der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Abh. d. Bunsen Gesellschaft	Abhandlungen der Bunsen Gesellschaft.
Ahrens Sammlung	Ahrens Sammlung.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Physiol.	American Journal of Physiology.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Physik	Annalen der Physik.
Arch. d. Sci. Phys. et Nat. Geneva	Archives de Sciences Physiques et Naturelles, Geneva.
Arch. Inst. Physiol.	Archives de l'Institut de Physiologie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. Chem. Phys. u. Path.	Beitrage Chemische Physik und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Biochem. Zeitsch.	Biochemische Zeitschrift.
B.P.	British Patent.
Bull. Acad. Sci. Cracow	Bulletin International de l'Académie des Sciences de Cracovie.
Bull. Acad. Roy de Belgique	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Bur. of Standards	Bulletin of the Bureau of Standards (U.S.A.).
Bull. des Sciences Technol	Bulletin des Sciences et Technologie.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull Soc. Ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. de Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.

ABBREVIATED TITLE.	JOURNAL.
D.R.P.	Deutsches Reichs-Patent.
Edin. Phil. J.	Edinburgh Philosophical Journal.
F.P.	French Patent.
Gazzetta	Gazzetta chimica italiana.
Jahresber.	Jahresberichte über die Fortschritte der Chemie.
Jahresber. Ges. vaterl. Kultur	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chem. Soc.	Journal of the Chemical Society.
J. f. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung.
J. Gas Lighting	Journal of Gas Lighting.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Pet. Tech.	Journal of the Institute of Petroleum Technologists.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Monatsh.	Monatshefte für Chemie und yerwandte Theile anderer Wissenschaften.
Petroleum Zeit.	Petroleum Zeitung.
Pflüger's Archiv	Archiv für das gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Phil. Mag.	Philosophical Mazagine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Ann.	Poggendorff's annalen der Physik und Chemie.
Proc. Amer. Gas. Inst.	Proceedings of the American Gas Institute.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Paint Varnish Soc.	Proceedings of the Paint and Varnish Society.
Proc. Phys. Soc. London.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Quart. J. exp. Physiol.	Quarterly Journal of Experimental Physiology.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Schweigger's Journ.	Schweigger's Journal für Chemie und Physik.
Seifenfabrikant	Der Seifenfabrikant.
Seifen Zeit.	Seifensieder Zeitung.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Kaiserliche Akademie der Wissenschaften in Wien.

Abbreviated Title.	Journal.
Sitzungsber. K. Akad. München	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zü München.
Soc. Tech. de l'Ind. du Gaz en France	Société Technologique de l'Industrie du Gaz en France.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Farad. Soc.	Transactions of the Faraday Society.
U.S.P.	United States Patent.
Virchow Archiv	Virchow Archiven.
Wied. Ann.	Wiedemann Annalen der Physik und Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. f. Beleucht.	Zeitschrift für Beleuchtung.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für Physiologische Chemie.

All temperatures, unless otherwise stated, are in Centigrade.

CATALYSIS IN THEORY AND PRACTICE

CHAPTER I

EARLY HISTORY

THE conscious development of catalysis in chemical science dates from the co-ordination by Berzelius, in 1835, of a number of isolated observations made by various investigators in the early decades of the nineteenth century. Berzelius for many years contributed annually to the Swedish Academy of Sciences a report on the progress of the physical sciences during the preceding year. The communication of March, 1835, subsequently published as the *Jahresberichte für Chemie*, 1836, contained, *inter alia*, a discussion of the researches of Mitscherlich[1] on the *rôle* of sulphuric acid in the preparation of ether from alcohol. It was shown by Berzelius that the results of this investigation possessed features common to several investigations of the most diverse character.

The argument as developed by Berzelius may be briefly summarised.[2] "Up to 1800, it was recognised that, besides the normal tendency of bodies to combine, heat and in some cases light could also act in the process of combination. Later, the influence of electricity was recognised, but it was soon seen that chemical and electrical affinities were the same thing, and that heat and light had no other action than to augment and diminish these affinities." A new type of force was involved, however, according to Berzelius, in a number of reactions. Thus Kirchhof had shown[3] that in the con-

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[1] *Pogg. Ann.*, 1834, **31**, 273.

[2] *Jahresber.*, 1836, **15**, 237 ; *Ann. Chim. Phys.*, 1836, (iii), **61**, 146.

[3] *Schweigger's Journ.*, 1812, **4**, 108.

version of starch to sugar by means of dilute acids, the acid effecting the change remained unaltered. Thenard discovered hydrogen peroxide and showed that in presence of acids the substance was stable. With alkali, however, decomposition set in with evolution of oxygen, which was also facilitated by the presence of substances such as manganese, silver, platinum, gold, and fibrin.[1] Edmund Davy[2] demonstrated that with finely divided platinum soaked in spirit of wine ethyl alcohol was oxidised to acetic acid. In 1822 Döbereiner[3] showed that spongy platinum in the cold induced the spontaneous combustion of hydrogen and oxygen, and this observation was followed by the discovery of Dulong and Thenard [4] that gold, silver, and even glass possessed the same property if the temperature of these agencies was sufficiently raised. Finally, cites Berzelius, the researches of Mitscherlich show that the conversion of alcohol to ether was not dependent on the affinity of sulphuric acid for water, since by a proper adjustment of conditions the addition of alcohol to sulphuric acid resulted in the evolution of ether and water, the sulphuric acid therefore being analogous to the alkali of Thenard in the decomposition of hydrogen peroxide.

Berzelius therefore concludes: "It is then proved that several simple and compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they themselves remain indifferent.

"This new force, which was hitherto unknown, is common to organic and inorganic nature. I do not believe that it is a force quite independent of the electrochemical affinities of matter; I believe, on the contrary, that it is only a new manifestation of the same; but, since we cannot see their connection and mutual dependence, it will be more convenient to designate the force by a separate name. I will therefore call this force *the catalytic force*, and I will call *catalysis* the decomposition of bodies by this force in the same

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[1] *Ann. Chim. Phys.*, 1818, **9**, 314.

[2] *Phil. Trans.*, 1820, **100**, 108.

[3] *Schweigger's Journ.*, 1822, **34**, 91; 1823, **38**, 321.

[4] *Ann. Chim. Phys.*, 1823, (ii), **23**, 440; **24**, 380.

way that one calls by the name analysis the decomposition of bodies by chemical affinity."

The illustrations of catalysis cited by Berzelius in the memoir just quoted represented by no means an exhaustive list of the catalytic operations which had up to that time been used and studied. Obviously, many of the primitive arts involved unconsciously the application of Berzelius's "catalytic force." The production of wine, for example, by fermentation processes dates back to the ancients, though neither sugar nor alcohol appear to have been known, as such, to Pliny, Berthelot tracing back the rectification of alcohol from wine no further than the eighth century.[1] The production of acetic acid by fermentation of wine gave the ancients their earliest acid solvent. The manufacture of soap by the action of alkalis on fats also dates back to ancient times. Pliny[2] refers to "Sapo, Gallorum hoc inventum," and makes it probable that the Romans received from Gaul and Germany a product prepared from animal fat and the aqueous extract of ashes. Ether, which has been attributed to the Arabians, was certainly well known in the Middle Ages, being produced by the action of sulphuric acid on alcohol. The first exact knowledge of its preparation we owe to Valerius Cordus in the sixteenth century. The mineral acids were not known until the alchemical era, but the preparation of sulphuric acid by setting fire to sulphur admixed with saltpetre is the alchemical origination of the catalytic lead chamber process of sulphuric acid manufacture. The identity of the sulphuric acid obtained by the different methods of preparation from alum, from vitriol, and from sulphur and nitre was established by Libavius in the Iatro-Chemical era, to whom is also to be attributed the first use of the term "catalysis" in a chemical treatise. In the table of contents of his treatise on Alchymia is to be found a section devoted to "Catalysis," but, according to Goldschmidt,[3] examination of the treatise itself fails to reveal anything corresponding with that implied in our modern use of the term. One cannot entirely dissociate the alchemist's search for the "philosopher's stone" from the modern search for suitable catalysts. George

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[1] *Ann. Chim.*, 1852, (vi), **23**, 433.

[2] *Hist. Nat.*, **28**, 12.

[3] *Zeitsch. Elektrochem.*, 1903, **9**, 736.

Ripple likened the stone to a ferment. The records of the efficacy of the philosopher's stone in the literature of alchemy suggest, moreover, the poisoning of catalysts with which, later, this volume will be largely concerned. Thus, Roger Bacon ascribes to the stone the power to transform a million times its weight of base metal into gold. The more audacious Raymond Lully cites the transformation of ten billion times its weight of base metal. But, with the decay of alchemy, the claims become more modest, or the poisoning effect becomes the more pronounced, for John Price, the last alchemist and gold-maker of the eighteenth century, is but able to chronicle an efficacy of thirty times and one of sixty times the weight of the stone.

Of researches prior to and in the early decades of the nineteenth century concerned with the operation of a catalytic agent and not included in the co-ordination of Berzelius, particular mention might be made of the following. Mrs. Fulhame[1] dealt with the influence of water on chemical reaction, more especially in the reduction of metallic oxides and in the oxidation of carbon monoxide, and clearly demonstrated the necessity for the presence of water, at least in traces, for the production of reaction. The researches of Döbereiner on the combustion of hydrogen and oxygen were preceded by the observations of Sir Humphry Davy[2] on the capacity of platinum wires or foil heated to below redness to promote the combination of oxygen with coal-gas, cyanogen, hydrogen cyanide, alcohol, ether, or naphtha. Erman[3] showed that platinum at a temperature of 50° was sufficient to ignite a mixture of hydrogen and oxygen. Döbereiner's work on the action of cold platinum introduced into the gases was rapidly followed by that of Turner[4] on the action of platinum in promoting the combination of hydrogen with chlorine and other gases, and his unsuccessful attempts to cause preferential combustion.

Impurities such as hydrogen sulphide, ammonia, carbon disulphide, ethylene, and ammonium sulphide, were shown to inhibit the activity of platinum. "It was this inefficiency

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[1] "An Essay on Combustion," London, 1794.

[2] *Phil. Trans.*, 1817, **97**, 45.

[3] *Abh. Akad. Wiss. Berlin*, 1818-19, 368.

[4] *Edin. Phil. Journal*, 1834, **11**, 99, 311.

of the platinum sponge on the compounds of charcoal and hydrogen in mixture with oxygen, while it reacts so remarkably with common hydrogen, and also, though slowly, on carbonic oxide," that suggested to Henry[1] "the possibility of solving by its means some interesting problems in gaseous analysis. I hoped more especially to be able to separate from each other the gases constituting certain mixtures, to the compositions of which approximations had hitherto been made, by comparing the phenomena and results of their combustion with those which ought to ensue, supposing such mixtures to consist of certain hypothetical proportions of known gases." And the conclusion is drawn that, "When the action of the platinum sponge was moderate, only the hydrogen and carbonic oxide were consumed, or at most the olefiant gas was but partially acted upon. From the facts which have been stated, it appears that when the compound combustible gases, mixed with each other, with hydrogen, and with oxygen are exposed to the platinum balls or sponge, the several gases are not acted upon with equal facility ; but that carbonic oxide is most disposed to unite with oxygen ; then olefiant gas, and, lastly, carburetted hydrogen. By due regulation of the proportion of hydrogen it is possible to change the whole of the carbonic oxide into carbonic acid without acting on the olefiant gas or carburetted hydrogen." At a temperature of 170° it was further shown by Henry that "when carbonic oxide and hydrogen gases in equal volumes, mixed with oxygen sufficient to saturate only one of them, were placed in contact with the sponge, from the quantity of carbonic acid remaining at the close of the experiment it appeared that four-fifths of the oxygen had united with the carbonic oxide and only one-fifth with the hydrogen," a remarkable result, which was also obtained when excess was used. This extraordinary research represents in many respects a study of catalytic action of the most fundamental importance even at the present day.

The genesis of the modern contact process of sulphuric acid manufacture dates also from the period prior to the Berzelian definition of catalysis. Phillips, a Bristol manufacturer of vinegar, patented[2] the use of platinum, whether of

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[1] *Phil. Mag.*, 1825, **65**, 269.

[2] B. P., 6069/1831.

wire or sponge, for the oxidation of sulphur dioxide by means of air. The process was employed at Lille by Kuhlmann in 1883, but was abandoned owing to loss of catalytic activity by the platinum, an inhibiting factor which was not satisfactorily overcome in technical practice until the dawn of the present century.

It is to Faraday[1] that we owe a detailed inquiry into "the power of metals and other solids to induce the combination of gaseous bodies" and into "some very extraordinary interferences with this phenomenon." The researches were initiated in the course of experiments to render efficient the hydrogen-oxygen voltameter, in which Faraday "was occasionally surprised at observing a deficiency of the gases resulting from the decompositions of water, and at last an actual disappearance of portions which had been evolved, collected and measured. . . . It was found that this effect was not due to the escape or solution of the gas, nor to recombination of the oxygen or hydrogen in consequence of any peculiar condition *they* might be supposed to possess under the circumstances; but to be occasioned by the action of one or both of the (platina) poles within the tube upon the gas around them." It was established that the positive platina plate was more active than the negative, and that with the former, in addition to its rapid action on oxygen and hydrogen, a feebler action was exerted by it on mixtures of nitrous oxide and hydrogen. According to Faraday, mixtures of olefiant gas or carbonic oxide with oxygen, or of equal volumes of hydrogen and chlorine, were not affected by the prepared platina plate.

"Reverting to the action of the prepared plates on mixtures of hydrogen and oxygen, I found that the power, though gradually diminishing in all cases, could still be retained for a period varying in its length with circumstances. . . . The continuance of the action greatly depended upon the purity of the gases used. . . . The act of combination always seemed to diminish, or apparently exhaust, the power of the platina plate."

As a result of his inquiries Faraday concludes that it may

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[1] "Experimental Researches in Electricity," 1849, **1**, 165, 6th series, Nos. 564–659; "Everyman's Library," No. 576, pp. 84–111; *Phil. Trans.*, 1834, **114**, 55.

be observed of this action, that, with regard to platina, it cannot be due to any peculiar, temporary condition, either of an electric or any other nature: the activity of plates rendered either positive or negative by the pole, or cleaned with such different substances as acids, alkalis, or water; charcoal, emery, ashes, or glass; or merely heated, is sufficient to negative such an opinion. Neither does it depend upon the spongy and porous, or upon the compact and burnished, or upon the massive or attenuated state of the metal, for in any of these states it may be rendered effective or its action taken away. The only essential condition appears to be a *perfectly clean* and *metallic surface,* for, whenever that is present the platina acts, whatever its form and condition in other respects may be; and though variations in the latter points will very much affect the rapidity, and therefore the visible appearances and secondary effects of the action; *i.e.* the ignition of the metal and the inflammation of the gases, they, even in their most favourable state, cannot produce any effect unless the condition of a clean, pure, metallic surface be also fulfilled.

"All the phenomena connected with this subject press upon my mind the conviction that the effects in question are entirely incidental and of a secondary nature; that they are dependent upon the *natural conditions* of gaseous elasticity combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction. I am myself prepared to admit (and probably many others are of the same opinion) both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance: and I think that this kind of attraction is a determining cause of Döbereiner's effect, and of the many others of a similar nature."

It will be evident, therefore, that Faraday, in 1833, and prior to the co-ordination by Berzelius of the several examples of catalytic action, had clearly expressed a theory as to the mechanism whereby such action should occur. The theory, it will be observed, confirms the viewpoint expressed by Berzelius in his later publication, that the catalytic force is not independent of the affinities of matter but only a new manifestation of the same.

The retardation caused by admixture of foreign gases on the combination of hydrogen and oxygen was also studied by Faraday, who found that "the order in which carbonic acid and these substances seemed to stand was as follows, the first interfering least with the action; nitrous oxide, hydrogen, carbonic acid, nitrogen and oxygen." These did not prevent the action of the plates, "nor was the retardation so great in any case as might have been expected from the mere dilution of the oxygen and hydrogen." Faraday found that ethylene decreased the action of platinum more than did carbon monoxide; but this result was not confirmed by Henry[1]; Bancroft[2] thinks this was probably due to some impurity in Faraday's ethylene. The retardation by carbon monoxide, however, is well confirmed by both investigators.

Of the explanation of retardation, Faraday writes: "The theory of action which I have given for the original phenomena appears to me quite sufficient to account for all the effects by reference to known properties, and dispenses with the assumption of any new power of matter. I have pursued this subject at some length, as one of great consequence, because I am convinced that the superficial actions of matter whether between two bodies, or of one piece of the same body, and the actions of particles not directly or strongly in combination, are becoming daily more and more important to our theories of chemical as well as mechanical philosophy. In all ordinary cases of combustion it is evident that an action of the kind considered, occurring upon the surface of the carbon in the fire, and also in the bright part of the flame, must have great influence over the combinations there taking place."

The student of catalysis no less than, for other reasons, the

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[1] *Phil. Mag.*, 1836, (iii), **65**, 329.

[2] *J. Phys. Chem.*, 1917, **21**, 755.

student of electro-chemistry, is deeply indebted to Faraday for this early orientation into the mechanism of catalytic action.

The isolation by Payer and Persoz[1] of the enzyme diastase from the extract of barley malt was succeeded by the discovery of emulsin in bitter almonds by Liebig, and the formulation of a theory of its mode of action, which, however, in view of the preceding review of Faraday's work, is wrongly stated by Ostwald[2] to be the first theory of catalytic action.

In propounding a theory of catalytic action Liebig was animated with the purpose of demonstrating that the Berzelian concept of a special catalytic force was superfluous. As originally expressed, the cause of catalytic action lay in the facility possessed by a body in decomposition or combination of communicating to another body in contact with it the same chemical activity or the same powers of combination which the body itself possessed. In illustration of this property, Liebig cited the combustion of a body by bringing it into contact with a body which is itself undergoing combustion, and in further illustration, the solubility of platinum when alloyed with silver in acids in which normally the platinum alone remains insoluble.

The illustrations chosen by Liebig can scarcely be described as happy, since as Berzelius very readily pointed out,[3] numerous researches had already shown that a burning body was not necessary for the production of combustion. Even cold platinum sponge was sufficient to bring about the ignition and also explosive combustion of hydrogen and oxygen. On the other hand, the solubility of platinum when alloyed with silver was not to be explained on Liebig's assumptions, since, as Berzelius emphasised, solution of platinum was not effected when present in alloys with iron, copper, zinc, or mercury.

Liebig was therefore constrained to modify his theory of catalytic action, and did so in reference to the problem of sugar fermentation. The hypothesis became one of "molecular vibrations," communicable, by contact, to another body,

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[1] *Ann. Chim. Phys.* 1833, (ii), **53**, 73,

[2] "Uber Catalyse, Vers. Ges. Deutsch. Naturforscher und Arzte," Hamburg, 1901.

[3] *Jahresber.*, 1841, **20**, 452.

thus setting up in the atoms of the second system similar motions leading to reactions or decomposition. In the particular case of sugar fermentation, this would involve that the decomposing yeast-cells, in the process of decomposition induce instability in the molecules of sugar which thereby suffer accelerated decomposition to alcohol and carbon dioxide.

The disadvantage of the Liebig theory lies in its unassailability since no possible test of the theory can readily be devised. It is comprehensive, and as such has earned considerable popularity, owing to its applicability to numbers of imperfectly understood reactions ; but, as Ostwald pointed out[1] it is of but little use as an auxiliary to scientific research, for the direction and suggestion of new lines of investigation. The theory called forth the following caution from Berzelius : In science, one always loses by plausible explanations published prematurely ; the only correct method of attaining certain knowledge is to be found in leaving the incomprehensible until the explanation sooner or later is given by facts which are so clear that divided opinion upon the matter can scarcely arise. The procedure thus recommended by Berzelius was faithfully exemplified in the researches of Schönbein, to whom is due many of the facts of the problem of catalysis which we at present know, but who partook to no extent in the theoretical discussions as to cause.

The action of oxides of nitrogen in the lead chamber process possesses considerable historical interest in regard to catalysis since the explanation originally put forward by Clément and Désormes[2] involving a series of cyclic reactions, the alternate formation and decomposition of "chamber crystals," may be regarded as the first attempt to explain a catalytic process by what has come to be termed the intermediate compound theory. In all the early discussions of the nature of catalytic processes this case was apparently overlooked. The corresponding explanation of the etherification process by Williamson in 1854,[3] involving the intermediate formation and subsequent decomposition of ethyl sulphuric acid, established the concept of intermediate compound formation and led eventually to its extended application to the theoretical

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[1] *Loc. cit.*

[2] *Ann. Chim.*, 1806, **59**, 329.

[3] *Ann. Chim. Phys.*, 1854, (iii), **40**.

interpretation of catalytic processes in which the stoichiometric relationships were not so definitely established.

In the development of a subject so intimately concerned as is catalysis with the conception of velocity of reaction the researches of Wilhelmy[1] entitled "On the Law according to which the Action of Acids on Cane-sugar Occurs," call for special reference. The importance of the researches lies in the fact that they were the first successful attempts to study the operation of the time factor in chemical reaction. Wilhelmy showed with reference to the hydrolysis of cane-sugar that the rate of inversion was at any moment proportional to the amount of cane-sugar undergoing transformation, in strict agreement with the mathematical equations which he developed from general considerations. The research moreover, is the first successful attempt to establish the law of mass action in a quantitative manner. Wilhelmy further studied the influence of temperature and concentration of acid in reference to reaction velocity, without, however, coming to any important conclusions. At the close of his research Wilhelmy remarks: "I must leave it to the chemists to decide, whether and how far the formulæ obtained are applicable to other chemical processes; in any case, all those processes to which one ascribes the operation of a catalytic force seem to me to belong to this class." As Ostwald has pointed out, the research was overlooked by numerous later investigators, and it was not until the attention of men of science had been directed to the work by Ostwald[2] that it was recognised that Wilhelmy is to be designated the discoverer of the laws of chemical reaction velocity, since the formulæ which he put forward were subsequently shown to be applicable to a number of chemical processes. The extension of Wilhelmy's work was undertaken by Löwenthal and Lennsen,[3] who showed that the velocities with which the acids invert cane-sugar is proportional to the strengths of the acids. The influence of temperature on reaction velocity was successively studied by Berthelot,[4] by Harcourt and

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[1] *Pogg. Ann.*, 1850, **81**, 413, 499.

[2] *J. pr. Chem.*, 1884, **29**, 385.

[3] *Ibid.*, 1862, (i), **85**, 321, 401.

[4] *Compt. rend.*, 1864, **59**, 616 *et seq.*; *Ann. Chim. Phys.*, 1869, (iv), **18**, 146.

Esson,[1] and later still by Warder,[2] Urech,[3] van't Hoff, Arrhenius, and many others.

Ostwald claims to have introduced the concept of reaction velocity as a definite criterion of a catalytic process by his insistence, since 1888, on the point of view that the catalyst is to be regarded as accelerator (or inhibitor) of a reaction already taking place, in contradistinction to the concept that a catalyst can initiate a reaction. In agreement with this idea, the following definition of catalysis was put forward by Ostwald: "Catalysts are substances which change the velocity of a given chemical reaction without modification of the energy factors of the reaction." [4] It is claimed by Ostwald for this change, slight though it appears, that it has yielded important results in the scientific development of the subject, since it has facilitated exact investigation of the magnitude and character of such acceleration. It will be shown, however, in the succeeding chapter, that the point of view thus put forward does not enjoy universal acceptance. Schönbein, J. J. Thomson, H. E. Armstrong, and Duhem have all indicated their opinion that a catalyst may actually initiate a reaction.

Of the early efforts in the study of catalysis there remain for consideration those which have reference to the influence of the catalyst on reversible processes. As early examples among these may be cited the researches of Lemoine[5] on the decomposition of hydriodic acid as a type of a heterogeneous catalysis, and those of Berthelot[6] on the equilibria attained in esterification processes, as a type of homogeneous catalysis.

Lemoine demonstrated that in presence of platinum sponge the decomposition limit at 350° was 19 per cent., attained practically immediately. On the contrary, operating without a catalyst at the same temperature under a pressure of two atmospheres, a limit of 18·6 per cent. decomposition was attained, although only after an interval of 250 to 300 hours.

Berthelot established the same independence of the equili-

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[1] *Phil. Trans.*, 1867, **167**, 117.

[2] *Amer. Chem. Journ.*, 1881, **3**, 203.

[3] *Ber.*, 1883, **16**, 762; 1884, **17**, 2165; 1887, **20**, 1836.

[4] *Chemische Betrachtungen*, "Die Aula," 1895, No. 1.

[5] *Ann. Chim. Phys.*, 1877, (v), **12**, 145.

[6] *Bull. Soc. chim.*, 1879, **31**, 342.

brium state in the esterification of alcohols by acetic acid in the absence, and in presence, of traces of mineral acid catalysts such as hydrochloric or sulphuric acid. At the ordinary temperature the equilibrium state was reached with equivalent initial concentrations of alcohol and acid when 66 per cent. of the alcohol had been converted in either case, the time required, however, involving years of contact in the absence of catalyst as opposed to a few hours in presence of the mineral acid. In the subsequent theoretical discussion it will emerge that the *rôle* of the catalyst in the question of equilibrium has a very considerable significance, and has therefore been the object of numerous investigations. The manifold directions which these have assumed necessitate special and individual treatment not consonant with an historical survey, and consequently further discussion will not be intruded at this juncture.

From 1880 onwards the studies of catalytic reactions rapidly multiplied. They were concerned with all the many-sided aspects of the problem. On one hand, investigations yielded advance in the knowledge of theoretical principles underlying catalytic change. On the other, carefully conducted investigations added to the list of reactions capable of catalytic acceleration, a list which, judging by the investigations of Thenard,[1] on hydrogen peroxide decomposition, or by the speculations of Ostwald might well become comprehensive of all chemical reactions. Catalytic processes were employed with signal success in the studies inaugurated by the theory of electrolytic dissociation of Arrhenius and in the development of modern physical chemistry which resulted from that theory and the theory of dilute solutions of van't Hoff. At the same time there was developing, constantly and consciously, the application of catalysis to industrial enterprise, which has yielded results the importance of which can be adjudged from a consideration of the manufacture of synthetic indigo, of contact sulphuric acid, of synthetic ammonia, or of the modern hydrogenation of fats.

It is to the many features of all such developments that attention will, in the succeeding chapters, be directed.

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[1] *Ann. Chim. Phys.*, 1818, **9**, 314.

CHAPTER II

THEORETICAL INTRODUCTION

CRITERIA OF CATALYSIS

In the preceding chapter relative to the early history of catalysis it has been shown that a large number of reactions proceed in the presence of suitable agents, which, following the nomenclature of Berzelius, are called catalytic agents, the reactions themselves being spoken of as examples of catalysis. Thus far, however, no exact definition of catalytic action has been laid down, and little has been said as to criteria of catalysis beyond the definition attributed to Ostwald, in which the acceleration of a reaction by the presence of a given substance is regarded as a criterion of catalytic action. In order, therefore, to delimit the field of chemical science with which this survey is concerned, it is necessary to proceed to an examination of the various tests which may be applied to a given chemical operation in order to ascertain whether, in the process thereof, the phenomenon of catalysis intrudes. The criteria thus laid down it will be advantageous to illustrate by reference to typical examples and to the research work which has been conducted with a view to verification.

A close analysis of the examples which have already been cited would lead to a general conclusion which, as a first criterion of catalytic processes, may be stated thus: *The chemical composition of the catalytic agents is unchanged on completion of the reaction process.*

In the case of heterogeneous catalytic reactions, as, for example, the early experiments on the catalytic combustion of various gases in presence of platinum, this criterion is the more readily obvious. The metal catalyst can be employed successively to bring about reactions between successive quantities of the gases, with the proviso, however, to be discussed more in detail somewhat later, that in the operation of the process the absence of materials which prevent the action of the catalyst is ensured.

In homogeneous systems, while not so obvious, the same criterion holds. So long ago as 1812 Kirchhof demonstrated its validity in reference to the hydrolysis of starch by employment of dilute acid catalysts. It was shown that, after completion of the hydrolytic process, the acid remained in the system in its original concentration and could be employed to produce hydrolysis of further quantities of the substrate.

Stress must be laid on the statement that the unchangeability of the catalyst is limited to its chemical composition. In regard to its physical state, this does not hold. Numerous examples could be cited in heterogeneous catalysis to illustrate the change in physical state of the catalyst with participation in catalytic change. Döbereiner's platinum wire becomes covered, after reaction, with a finely divided deposit of metallic platinum, or corroded or pitted in the process of catalysing the hydrogen-oxygen combination. The same phenomenon is observed in the case of the platinum wire forming the gauze used as catalyst in the modern technical process for the oxidation of ammonia with air or oxygen, and Bone has illustrated its occurrence in the employment of silver gauzes in surface combustion processes.

The change in physical state of the catalyst is generally attributed to its activity in a series of cyclic actions in which the material participates, the final reaction of the cycle resulting however in the regeneration of the catalytic material in its initial form. Thus, in the well-known action of manganese dioxide in promoting the decomposition of potassium chlorate with evolution of oxygen, it has been observed that, if, initially, a crystalline form of the oxide be employed the final product is manganese dioxide in the form of a fine powder. The researches of Sodeau[1] have associated this change in physical state with the participation

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[1] *J. Chem. Soc.*, 1900, 77, 137, 717; 1901, **79**, 247, 939; 1902, **81**, 1066.

by the manganese oxide in the process of chlorate decomposition.

The change in physical state is also frequently associated with a change in the activity of the catalytic material. Copper oxide increases considerably in the activity with which it promotes combustion processes by prolonged use. Thus the temperature at which the combustion of hydrogen and oxygen commences is considerably lowered by continued use of the same sample of catalyst, with the result that the reaction may easily be brought about at temperatures below 100° with a sample the physical state of which has been suitably changed in process of operation. Consequently, in the definition of the catalytic activity of a given material the emphasis to be laid on the physical state of the catalyst is necessarily of prime importance. Massive oxide of iron as it occurs in certain minerals acts but indifferently, and only at comparatively high temperatures, as a catalyst in promoting the reaction between carbon monoxide and steam,

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

a reaction which is made use of in the modern catalytic process for the manufacture of hydrogen from water-gas. On the other hand, the porous oxide of iron obtained by low temperature calcination of spathic iron ore, or the porous mass obtained by reduction of iron by means of charcoal, possesses marked activity in promoting the chemical reaction at much lower temperatures.

A second criterion of catalytic action may now be stated, a consideration of which will reveal that it is a corollary of that already formulated: *minimal amounts of a catalytic agent are adequate for the transformation of large quantities of the reacting substances.*

Since the chemical composition of the catalytic agent is unchanged on completion of the reaction process, it follows that the process could be repeated as often as desired, and thus the necessity of this second criterion is demonstrable. So long ago as 1806, observation of the cyclic nature of the reaction of oxides of nitrogen in the lead chamber process of sulphuric acid manufacture led Clément and Désormes to this conclusion, which is universally valid in all cases in which the possibility of secondary reactions is excluded. These latter, however, are by no means infrequent, and so it is common in the literature of catalytic agencies to refer to the "life" of a catalyst. This may be stated in a variety of ways, all of which, however, are referable to the ratio of reactants transformed to catalytic material employed.

In illustration of the several points thus raised in connection with the quantity of catalyst required for the transformation of reacting substances, the following examples may be cited. Bredig has pointed out that the combination of hydrogen and oxygen at the ordinary temperature would be brought about by 2·5 c.c. of a colloidal solution of platinum containing as little as 0·17 milligram of platinum, and that at the outset the rate of combination was 1·8 c.c. of gas per minute. After a period of time during which 10 litres of gas had undergone combination, it was found that the activity of the colloidal solution was still unimpaired, the velocity of combination being, within the experimental error, identical with that prevailing at the commencement. Mellor[1] cites the observation of Titoff[2] that the presence of 0.000,000,000,000,1 $N.CuSO_4$ solution is sufficient to produce a perceptible acceleration of the rate of oxidation of an aqueous solution of sodium sulphite.

Sulphuric acid is the usual catalyst for the dehydration of alcohol to yield ether. As operated in modern technical practice, secondary reactions are practically excluded, so that an initial quantity of sulphuric acid is sufficient for the transformation of large quantities of alcohol. In the laboratory, and also in less modern types of technical plant where the control of the process is by no means so certain, it is a matter of common observation that, in addition to the etherification process, side reactions intrude, manifested by charring of the organic material and reduction of the sulphuric acid to sulphur dioxide. In such circumstances the catalyst shows a steadily diminishing efficiency, so that sooner or later replacement of the acid becomes necessary. Such an example illustrates the importance of the problem of side-reactions to the main catalytic process in the technical application of catalysis. It will emerge later in the discussion on "catalyst

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[1] "Chemical Statics and Dynamics."

[2] *Zeitsch. physikal. Chem.*, 1903, **45**, 641.

poisons" that in such cases as the contact sulphuric acid process, the synthesis of ammonia and its oxidation to nitric acid, as well as in many other reactions of technical importance, the essentials of success are to a considerable degree governed by the elimination of materials which by reaction with, or modification of, the catalytic material, suppress practically entirely the activity of the catalyst.

Accepting the two criteria of catalysis already laid down, it is possible, with the aid of the laws of thermodynamics, to proceed to the formulation of yet other criteria. According to the two laws of thermodynamics, the energy change associated with the transformation of a given reacting system is a function of the initial and final states of the system, independent of the path taken by the reacting substances in the attainment of the end state. This is merely another method of stating the law of conservation of energy, for, were conditions otherwise, it would be possible to arrange a cycle of operations in which a given reaction could be conducted by one path and reversed by another, with which, therefore, unless the energies required via the two paths were identical, a positive yield of energy could be continuously obtained. In other words, a *perpetuum mobile* would result. Now, since at the end of a catalytic reaction, the catalyst remains unchanged in chemical composition, the net energy contributed by the catalyst to the reacting system must be zero. There follows, consequently, the conclusion that the energy factors governing the reaction which is catalysed remain identical in presence or absence of a catalytic substance. Now the position of equilibrium of a given reacting system is determined by the energy transformed in the process according to the well-known equation of van't Hoff :

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

where K is the equilibrium constant,
Q the heat of reaction at the absolute temperature, T,
R the gas constant (=2 cal.).

The conclusion is therefore inevitable that *a catalyst cannot affect the final state of equilibrium.*

This deduction may also be established after the manner of van't Hoff[1] in the following wise: "Theoretically, too, assuming that contact actions affected the equilibrium, we should come upon a *perpetuum mobile*, by working alternately with and without the contact substance; the conversion might thus be carried backwards and forwards indefinitely, and so work might be accomplished in a way, without fall of temperature, in contradiction to the laws of thermodynamics."

It must be emphasised that this conclusion involves acceptance of the criterion of catalysis that the catalyst remains unchanged. Where possibility of side reactions enters, apparent exceptions to this conclusion are found, as will be shown in the examples which follow.

Since the energy change accompanying a reaction is a measure of the driving force of the reaction, and since this is not modified by the presence of a catalyst, although, with this latter present, profound modifications in the velocity of reaction may occur, it follows that the catalyst must act in modifying the resistance of the system to the process of reaction. Ostwald compares the action of a catalyst, therefore, with the influence of oil on the wheels of a machine. The energy of the drive is not altered by the process of oiling, but merely the resistance. Similarly, the function of a retarding agent may be compared with the action of grit in the machine.

In any reversible action,

$$A + B \rightleftarrows C + D,$$

the condition of equilibrium may be referred to the rates at which the reaction proceeds in the two directions. In the one case, the reaction velocity is proportional to the concentrations of A and B,

$$r_1 \propto [A]\,[B] = k_1\,[A]\,[B],$$

and in the reverse change to the concentrations of C and D,

$$r_2 \propto [C]\,[D] = k_2\,[C]\,[D]$$

At equilibrium, the rates of the two reactions are identical, and hence

$$k_1\,[A]\,[B] = k_2\,[C]\,[D].$$

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[1] "Lectures on Theoretical Chemistry," 1898, p. 215.

So that the equilibrium constant,

$$K = \frac{[A]\,[B]}{[C]\,[D]} = \frac{k_2}{k_1}.$$

Now since the catalyst cannot affect the final state of equilibrium, it is obvious that the ratio k_2/k_1 is also independent of the catalyst, and so it may be concluded that *a catalyst modifies the velocity of two inverse reactions to the same degree.*

As a corollary to these two conclusions as to the state of equilibrium, it follows of necessity that the state of equilibrium is independent of the nature and quantity of the catalytic agent.

The researches of Lemoine on the equilibrium obtaining in the decomposition of hydrogen iodide, and those of Berthelot on the equilibrium in the esterification of carboxylic acids in presence of traces of mineral acid catalysts have already been cited in the historical introduction with reference to the influence of the catalyst on the position of equilibrium. Numerous additional examples could be given in support of the several criteria just outlined. Thus the equilibrium in the reversible transformation of acetone to diacetonyl alcohol was most carefully investigated by Koelichen,[1] who found that the reaction,

$$2CH_3{\cdot}CO{\cdot}CH_3 \rightleftarrows CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}OH,$$

catalytically accelerated by hydroxyl ions, attained the same equilibrium state from either side with such varied agents as ammonia, triethylamine, tetraethyl ammonium hydroxide, and sodium hydrate. Of reactions catalysed by acids, Henry[2] investigated the equilibrium obtaining in the conversion of γ-oxybutyric acid to γ-butyrolactone, and obtained good velocity constants on the assumption that the catalyst accelerated the inverse reactions to an equal extent. Bodenstein[3] indicated the same in reference to a heterogeneous reaction, the formation and decomposition of hydrogen selenide,

$$H_2 + Se \rightleftarrows H_2Se,$$

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[1] *Zeitsch. physikal. Chem.*, 1900, **33**, 129.

[2] *Ibid.*, 1892, **10**, 98.

[3] *Ibid.*, 1899, **29**, 429.

the catalytic agent being molten selenium. Turbaba[1] varied the catalytic agent in the aldehyde-paraldehyde equilibrium, showing that with hydrochloric acid, sulphur dioxide, oxalic acid, zinc sulphate, and other agents the proportion transformed was independent of the nature and quantity of the catalytic agent.

Of apparent exceptions to the view that the catalyst can not alter the state of equilibrium of a system, reference may be made to the case of equilibrium in esterification processes and in the hydrolysis of esters, much investigation relative to this issue having centred round these examples.

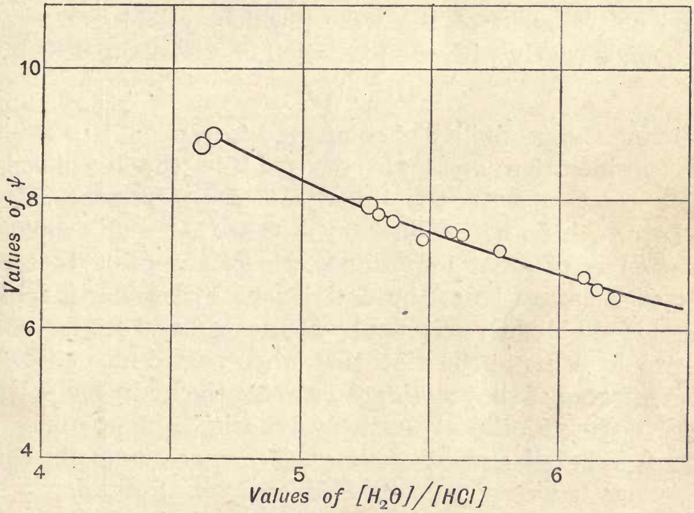

Fig. 1.

Jones and Lapworth[2] investigated the equilibrium constant in the hydrolysis of ethyl acetate using hydrochloric acid as catalyst. It was found that the value obtained varied according to the amount of catalyst employed. The appended diagram (Fig. 1) gives a plot of the values of the apparent equilibrium constant,

$$\psi = \frac{[H_2O][CH_3 \cdot CO \cdot OC_2H_5]}{[C_2H_5 \cdot OH][CH_3 \cdot COOH]},$$

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[1] *Zeitsch. physikal. Chem.*, 1901, **38**, 505.

[2] *J. Chem. Soc.*, 1911, **99**, 1427.

with different concentrations of acid. It will thus be seen that the value of ψ, obtained by Berthelot and Paen de St. Gilles for homogeneous liquid systems and in presence of traces of acid catalyst, rises steadily, with increasing concentration of hydrochloric acid, to values in the neighbourhood of 9. It must necessarily be concluded, therefore, that in the equilibrium equation the values used to represent the concentrations of the reacting species cannot be taken as the actual masses of each substance present. Jones and Lapworth associate the rising constant with a diminution in the active mass of the water, which, calculation shows, corresponds nearly with the formation of a compound,

$$HCl \cdot 2H_2O.$$

Admitting the possibility of compound formation, it is evident that consideration must also be paid to the likelihood of similar reaction with the other substances present. Jones and Lapworth do not incline to the view that such compound formation is of great importance, since, according to earlier work of these authors, the activity of hydrochloric acid in alcohol is but slightly affected by acetic acid and ethyl acetate. This would point to the view that when passed into an equilibrium mixture of the reacting substances the hydrogen chloride would combine almost exclusively with the water. The work of Kendall and his colleagues[1] demonstrates, however, the strong tendency to ester-acid complex formation which would undoubtedly also be manifest in mixtures of the type employed by Jones and Lapworth.

The dependence of the equilibrium in the case of ester hydrolysis on the concentration of the catalyst is also the subject of investigation by Armstrong and Worley.[2] In these researches also the formation of acid-water complexes is assumed to account for the variation of equilibrium point as well as for the accelerating action of the acid.

Apparent exceptions to the conclusions as to equilibrium may also arise in cases where side reactions or alternative reactions occur. The several decompositions of hydroxylamine and of hydrazine studied by Tanatar[3] may be instanced

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[1] *J. Amer. Chem. Soc.*, 1916, **38**, 1712.

[2] *Proc. Roy. Soc.*, 1912, [*A*], **87**, 604.

[3] *Zeitsch. physikal. Chem.*, 1902, **40**, 475; **41**, 37.

in this connection. A hot aqueous solution of hydroxylamine yields on decomposition ammonia, nitrogen, and water, with traces of nitrous oxide. If platinum black be employed to accelerate the decomposition, the nitrogen evolution is slight and the main gaseous product is nitrous oxide. The explanation of this is simple if it be realised that the hydroxylamine is capable of decomposing in two ways :

$$(a)\ 3NH_2{\cdot}OH = NH_3 + N_2 + 3H_2O.$$
$$(b)\ 4NH_2{\cdot}OH = 2NH_3 + N_2O + 3H_2O.$$

A preponderating catalytic acceleration of the latter by platinum black would cause the increase in nitrous oxide concentration and the apparent displacement of the ratio of the reaction products. Similarly, hydrazine decomposes in three different ways according to the reactions :

$$6N_2H_4 = 8NH_3 + 2N_2$$
$$6N_2H_4 = 6NH_3 + 3N_2 + 2H_2$$
$$6N_2H_4 = 4NH_3 + 4N_2 + 6H_2$$

The first reaction predominates with hydrazine sulphate, the second with free hydrazine, and the third with alkaline solutions.

Sabatier and Mailhe[1] have investigated a similar example of alternative reactions in the decomposition of alcohols, the one a dehydration, the other a dehydrogenation process :

$$(a)\ C_2H_5{\cdot}OH \rightleftarrows C_2H_4 + H_2O$$
$$(b)\ C_2H_5{\cdot}OH \rightleftarrows CH_3{\cdot}CHO + H_2.$$

It is shown that with certain agents, such as thoria, reaction (*b*) is practically negligible, whilst, for example, with magnesium oxide the dehydration process does not occur. Other oxides show an action intermediate to these extremes and with which both ethylene and hydrogen are found in the gaseous products. Engelder[2] has shown that the presence of water vapour or of hydrogen in the incoming alcohol also determines the ratios of ethylene and hydrogen in the resulting decomposition productions. Two separate and distinct reactions are here involved, on each of which the catalyst chosen has

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[1] *Ann. Chim. Phys.*, 1910, (viii), **20**, 341.

[2] *J. Physical Chem.*, 1917, **21**, 676.

a specific influence, the velocity of each, moreover, being determined in part by the catalyst and also by the presence of the reaction products. It should not be possible, therefore, to mistake the phenomena occurring or to attribute the same to an influence of the catalyst on the equilibrium.

The solvent medium as catalyst.—In a discussion of the *rôle* of the catalyst in equilibrium reactions, it is opportune to take into account the part played by the solvent in chemical reactions, since in many respects the phenomena displayed are analogous to those occurring in simple catalytic processes. Especially in the property just alluded to, that of directing a reaction along a definite path, the solvent behaves in the same manner as a catalyst. The solubility factor accounts in large measure for the directional influence of the solvent. Thus in aqueous solution potassium iodide precipitates mercuric iodide from a solution of mercuric chloride. In acetone, on the contrary, mercuric iodide is soluble, and so addition of mercuric chloride solution precipitates potassium chloride from solutions of potassium iodide. The directive influence of the solvent is also marked in the researches of Bruner and his pupils[1] on the relative amounts of ring and side chain substitution products in various solvents. The velocity with which a chemical reaction in solution proceeds is also determined by the nature of the solvent medium. Thus, the classical researches of Menschutkin[2] on the influence of solvent on the rate of interaction of triethylamine and the ethyl halides, for example,

$$C_2H_5I + (C_2H_5)_3N \rightarrow (C_2H_5)_4NI,$$

demonstrated a marked influence of the solvent as revealed by the following table :

Solvent.	Velocity constant.	Dielectric constant of solvent.
Hexane	0·00018	2·6
Xylene	0·00287	2·6
Benzene	0·00584	2·6
Ethyl alcohol	0·0366	21·7
Methyl alcohol	0·0516	32·5
Acetone	0·0608	21·8
Benzyl alcohol	0·1330	10·6

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[1] *Bull. Acad. Sci. Cracow*, 1910, 516.

[2] *Ber.*, 1882, **15**, 1818 ; *Zeitsch. physikal. Chem.*, 1887, **1**, 611 ; 1890, **5**, 589 ; 1890, **6**, 41.

Various efforts have been made to associate the influence of the solvent with its electrical properties, as, for example, the dielectric constant of the medium, or the ionising power of the solvent in Bruner's investigations of substitution, but it can be seen even from the above table that such physical properties alone are inadequate to explain the whole effect.

Definitions of catalysis which only include the criteria of velocity change and unalterability of the catalyst at the end of the operation manifestly will include solvents as catalysts. Ostwald[1] expressly recognises this, and points out in this respect that all the various intermediate stages can be found between cases of solvent influence and cases in which a very small amount of added substance changes the reaction velocity. Ostwald considers that the differences between the two extremes are merely quantitative, and that a systematic study of catalysis should not exclude cases in which the acceleration is small.

It is obvious, however, that the function of the solvent is not in accord with the criteria of catalysis already laid down in respect of the equilibrium position of a reaction. From this point of view the case of the solvent must rather be regarded in a manner similar to that outlined in the treatment of ester hydrolysis and the influence of increasing concentrations of hydrochloric acid on the equilibrium position. The effects produced are connected with the presence of large concentrations of solvent which exerts its influence on the equilibrium of the reaction occurring, by itself interacting with the components of the reaction system. Van't Hoff has stated this point of view with great clearness.[2] The effect of the medium may be regarded as dual.

(1) A catalytic action affecting the two actions of a reversible process equally and having no influence on the final state of equilibrium.

(2) A specific action dependent upon the relation of the catalyst to each of the reacting substances.

That the position of equilibrium is independent of the solvent medium if the latter is without specific action on the

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[1] *Zeitsch. Elektrochem.*, 1901, **9**. 998.

[2] *Vorlesungen über Chem.*, 1895, **1**, 218; "Lectures on Theoretical Physical Chemistry," 1899, **1**, 221.

reacting substances is capable of thermodynamic proof. For, in any two reversible reactions :

$$n_1A_1 \rightleftarrows n_2A_2 \text{ and } n_1B_1 \rightleftarrows n_2B_2,$$

the conditions of equilibrium are given by the equations,

$$k_1[A_1]^{n_1}=k_2[A_2]^{n_2} \text{ or } n_1 \log [A_1]-n_2 \log [A_2]=K_A,$$

and

$$k_1[B_1]^{n_1}=k_2\ [B_2]^{n_2} \text{ or } n_1 \log [B_1]-n_2 \log [B_2]=K_B.$$

Expressing the algebraic summation of the several terms by the general sign Σ_n we have

$$\Sigma_n \log [A]=K_A \text{ and } \Sigma_n \log [B]=K_B \quad . \quad . \quad . \quad (1)$$

Now the ratio of the concentrations of a substance in two solvents is determined by the partition coefficient of the substance, provided that the molecular state of the latter is identical in the two solvents. Hence if $[A]$ and $[B]$ denote the respective concentrations and S_A and S_B the solubilities in each solvent A and B, it follows that

$$\frac{[A]}{S_A}=\frac{[B]}{S_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From equations (1) and (2) there naturally follows, therefore, that

$$K_A-K_B=\Sigma_n \log \frac{[A]}{[B]}=\Sigma_n \log \frac{S_A}{S_B},$$

or

$$K_A-\Sigma_n \log S_A=K_B-\Sigma_n \log S_B=K,$$

which means that K is the same whatever solvent is used.

Similarly, it follows that

$$\Sigma_n \log \frac{[A]}{S_A}=K,$$

which is the mathematical expression of the fact that the equilibrium constant, K, of a reaction is independent of the solvent if the concentrations of the reacting species are expressed in terms of the concentrations of the saturated solution. Buchbock[1] attempted to utilise this method of

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[1] *Zeitsch. physikal. Chem.*, 1897, **23**, 123 ; 1900, **34**, 229.

stating concentrations in his researches on the velocity of decomposition of carbon oxysulphide in solutions of various salts and acids, the reaction occurring being

$$COS + H_2O \rightarrow CO_2 + H_2S,$$

which, with excess of water, gives a velocity equation of the form

$$\frac{-d[COS]}{dt} = k[COS],$$

or, with the above method of expression,

$$\frac{-d[COS]}{dt} = k_1\frac{[COS]}{S_{COS}}.$$

From the ordinary velocity constants and the coefficient of absorption of carbon oxysulphide in the various solutions it was possible to determine the value of k_1. The results obtained in about twenty different aqueous solutions of acids and salts showed a fair agreement especially marked in groups of similar salts. The deviations, however, from identity in the values obtained for k_1 demonstrate that influences other than those considered in these deductions actually occurred.

Adherents to the theory that the function of the catalyst is to modify the reaction velocity have laid it down as a criterion of catalysis that "*a catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.*"

In such circumstances it is assumed, therefore, that all reactions which proceed in the presence of a catalyst must also occur, although possibly at an extremely slow speed, even in the absence of the catalyst. For example, since hydrogen and oxygen combine at the ordinary temperature under the influence of a Faraday platinum plate, it is assumed that hydrogen and oxygen alone will slowly combine when quite free from any catalyst at the ordinary temperature. Manifestly, an experimental test of such a viewpoint is a matter of considerable difficulty, for two reasons. The analytical detection of an extraordinarily slow process in the presence of an unlimited time factor is a matter of extreme difficulty; secondly, in view of the universality of catalytic action it would be difficult to devise an experimental test in which *all* catalytic agencies were excluded, since, as is frequently the case, even the walls of a containing vessel may exert a considerable catalytic influence.

There are many who urge, however, that the catalyst is capable of initiating a reaction. It does not seem to be impossible to realise a case in which by removal of a hindrance to the progress of a reaction a substance should be capable of initiating a reaction which, in absence of such a catalyst, would not occur. The mechanical analogue of such a case would be the starting of a machine due to the removal of grit from the bearings by means of oil.

Positive catalysis.—Modification by a catalyst of the reaction velocity may result either in an increase or a decrease of the rate at which the reaction occurs. The modification may be spoken of as *positive catalysis* when the reaction velocity with which a given process occurs is accelerated by addition of the catalytic agent. It is with examples of positive catalysis that the science of catalysis is primarily concerned, more especially in its practical aspects, since the economy in the time, and, correspondingly, the temperature factors, are the principal practical considerations.

The number of positive catalytic agents is extremely great, as a perusal of the following chapters will help to show. They comprise every type of substance, metals, oxides, salts, acids, and bases. Occasionally, the reaction as it develops gives rise to compounds which themselves accelerate the reaction. Such cases are examples of positive *autocatalysis*. They may be exemplified in the case of the hydrolysis of an ester, which reaction is greatly accelerated by acids and therefore may be hastened by the acid formed during the process of hydrolytic change. The acceleration which occurs in the solution of copper in nitric acid is a familiar example of the autocatalytic effect, the modification of the velocity of solution being ascribed to the nitrous acid produced during the action of the acid on the metal.[1]

Promoters.—The positive catalytic effect produced by a given substance in a given reaction may, it is found, be con-

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[1] Veley, *Phil. Trans.*, 1871, 182, 279.

siderably enhanced by the admixture with the catalyst of small quantities of other substances. Normally, the acceleration produced by a catalyst is proportional to the concentration of the catalytic agent present, as will be illustrated in numerous examples in the following pages ; in the case of two catalysts accelerating the same reaction, their double effect is frequently the same as if each were reacting singly. This is true, for example, when a mixture of colloidal platinum and gold takes part in the decomposition of hydrogen peroxide. But exceptions to this rule are common. Mercury and copper sulphates each accelerate the oxidation of aniline or naphthalene by concentrated sulphuric acid. Their joint effect is greater than the sum of their individual activities. More especially, however, in gas reactions accelerated by solid catalysts does the phenomenon referred to become pronounced. The modification of catalytic activity produced by even minute quantities of foreign materials is in many cases quite astonishing and exploitation of this factor has been most marked in recent practical applications of catalysis. This may be illustrated by a textual quotation from the Badische Co.'s English patent[1] on improvements in the manufacture of hydrogen by the water gas–steam catalytic process: "In the researches on the production of hydrogen from mixtures of carbon monoxide and steam, according to the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

we have found that the power of catalytic agents generally can be improved by the presence of certain bodies which may be termed *promoters*. We have found, for instance, that the activity of the catalytic agents, especially those consisting of, or containing iron, nickel, or cobalt, or oxides thereof, and also the catalytic activity of other metals or oxides even such as, by themselves, are less active, can be greatly increased by the addition of certain compounds or bodies to which, as aforesaid, may be given the name promoters. Thus the activity of catalytic agents consisting of or containing iron, nickel, or cobalt, or oxides thereof, can be greatly increased by the addition of oxygen compounds of chromium, thorium, uranium, beryllium, antimony, and

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[1] No. 27963/1913.

the like. Further, a catalytic agent consisting of or containing iron in admixture with less than its weight of nickel, particularly after working for a long time, yields better results than does either iron or nickel when employed by itself. . . . In many cases, particularly when using catalysts of weak activity, we prefer to employ as promoter a compound which differs considerably from the catalytic agent, in particular with respect to valency, chemical basicity, and capability of reduction. . . . The contact masses containing iron, as the catalyst agent, and a smaller quantity of nickel, as above described as promoter, bring about rapid and far-reaching conversion without the simultaneous formation of methane, even when a comparatively low temperature is employed and, as compared with pure nickel, are further characterised (especially when suitable oxides or oxy-compounds are employed as binding agents, or as promoters) by possessing greater stability and less sensitiveness to deleterious influences such as, for instance, fortuitous increase of temperature and impurities in the gas mixture.

As examples of such contact masses, the patent application contains, *inter alia*, the following :

(1) The mixture obtained by evaporation and ignition of a solution of 85 parts of iron nitrate and 15 parts of chromium nitrate.

(2) The mixture obtained by ignition from a solution of the ingredients : 40 parts of ferric nitrate, 5 parts of nickel nitrate, and 5 parts of chromium nitrate.

(3) A preparation obtained by solution, evaporation, and ignition of 194 parts of iron nitrate, 5 parts of ammonium bichromate, and 1 part of thorium nitrate.

Especially in this latter case is the principle of the promoter illustrated. It is clear from this example that a mixture containing, in the main, oxide of iron, with admixture of but 2·5 per cent. of chromium compounds and only 0·5 per cent. of ceria is claimed to have considerable superiority as catalyst over a contact mass containing iron oxide alone.

This method of activation of a catalyst by admixture of small quantities of promoters is being rapidly extended in technical applications, and already in such important industries as ammonia synthesis, ammonia oxidation by non-platinum catalysts, and contact sulphuric acid manufacture using base metal contact materials the use of promoters has been definitely claimed in the patent literature.

Thus far no theory put forward to account for the acceleration of reaction by minute quantities of promoters added to the main catalyst material is completely satisfactory. A possible mechanism, which, however, has received no experimental test, may be advanced by considering the case of ammonia synthesis from mixtures of nitrogen and hydrogen. Reduced iron is an available contact substance, the activity of which may be regarded as due to the simultaneous formation of the compounds, hydride and nitride, with subsequent rearrangement to give ammonia and unchanged iron. Or, maybe, the activity of the iron is due to simultaneous adsorption of the two gases. The particular mechanism of the catalysis is unimportant for the present considerations. Now such bodies as molybdenum, tungsten, and uranium have been proposed, among others, as promoters of the activity of iron. It is conceivable that these act by adjusting the ratio in which the elementary gases are adsorbed by or temporarily combined with the catalytic material to give a ratio of reactive nitrogen and hydrogen more nearly that required for the synthesis, namely, one of nitrogen to three of hydrogen. From the nature of the materials suggested as promoters, it would seem that they are in the main nitride-forming materials, which on the above assumption of mechanism would lead to the conclusion that the original iron tended to adsorb or form an intermediate compound with a greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The catalytic activity of reduced iron as a hydrogenation agent would tend to confirm this viewpoint.

In reference to this suggested mechanism it must be emphasised, however, that in such examples of "promotion" as require only minute quantities of added promoter the activity is more difficult to understand. With the case of ammonia synthesis, the promoters are added in marked concentrations. It is difficult to realise, however, that 0·5 per cent. of ceria or a concentration of one molecule of ceria among 200 molecules of iron oxide, in the example cited above in reference to catalytic hydrogen production, can so far "redress the balance" of adsorption or combination as to produce the marked increase in activity of which it is capable. It is obvious that in this phase of the problem there lies an exceedingly fascinating field for scientific investigation, with the added advantages that, being practically virgin territory, the harvest to be gained therefrom should be rich and abundant.

Negative catalysis.—In the main, the studies of catalysis have been concerned with the acceleration of reaction. Cases of retardation or of negative catalysis are, however, not less interesting and important from the theoretical point of view, whilst their influence in the prosecution of applied catalysis is becoming increasingly marked. In the previous chapter, it was shown that diminution of activity was noted in reference to the catalytic activity of platinum by Turner, Faraday, and others. Water vapour, which normally acts as an exceedingly efficient positive catalytic agent, acts as a retarder in the decomposition of ammonia,[1] and in the oxidation of phosphorus[2]; water acts also as retarding agent in esterification processes in alcoholic solutions, in the decomposition of diazo-esters in alcoholic acid solutions, and in the decomposition of oxalic acid. Oxygen retards the combination of hydrogen and chlorine, carbon monoxide, hydrogen sulphide, ammonia; carbon disulphide retards the rate of combination of hydrogen and oxygen. Bigelow[3] showed the inhibiting action of such substances as mannite, benzaldehyde, and benzyl alcohol on the rate of oxidation of sodium sulphite by atmospheric oxygen. Neutral salts retard the hydrolytic activity of weak acids as well as that of bases. The diminution of the activity of colloidal catalysts and of enzymes by the presence of even small quantities of certain substances, such as hydrogen cyanide, hydrogen sulphide and mercuric chloride, may also be treated as cases of negative catalysis, although frequently referred to as examples of "poisons," a subject which is more fully treated below. An interesting example of a practical use for a negative catalyst is to be found in the retardation of the spontaneous decomposition of hydrogen peroxide solutions by addition

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[1] Than, *Annalen*, 1864, **131**, 121.

[2] Van de Stadt, *Zeitsch. physikal. Chem.*, 1893, **12**, 329.

[3] *Ibid.*, 1898, **26**, 493; **27**, 585.

of such substances as hydrofluosilicic acid, sodium pyrophosphate, and various organic compounds.[1]

As in positive catalysis, so also in the case of inhibition, there arises the possibility of retardation due to one of the products of reaction. This phenomenon is termed *negative autocatalysis,* or, alternatively, *auto-retardation.* It may be exemplified by the researches of Müller[2] on the negative autocatalytic action of hydrobromic acid in the hydrolytic decomposition of bromosuccinic acid. A more recent case of the same type is the anticatalytic effect of the hydrobromic acid formed in the hydrolytic decomposition of bromopropionic acid, the mechanism of which has been most thoroughly investigated by Senter and Porter.[3]

The problem of the mechanism of negative catalysis is as important as that of positive catalysis, the theories for the explanation of which are set forth in the latter portions of this chapter. Briefly, however, it may be stated here that the general tendency of theory to account for negative catalysis is in the direction of assuming either a suppression of a positive catalyst by the retarder or a reaction between the negative catalyst and one of the constituents of the reaction under investigation. The repression of the hydrogen-ion concentration of the weak acid catalyst in ester hydrolysis, by addition of a neutral salt having an ion in common with the acid, may be cited in exemplification of the former in homogeneous catalysis. In heterogeneous catalysis, as in the Faraday plate, adsorption of the negative catalyst on the platinum would be a corresponding assumption.

Catalytic poisons.—The reduction in activity of solid catalytic agents by the presence of relatively small amounts of certain substances is generally referred to as "poisoning." Obviously this is but a special application of the general problem of negative catalysis. The subject has, however, attained a considerable importance owing to its frequent occurrence on the transfer of a catalytic process, perfectly practicable on the laboratory scale with purified materials, to the stage

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[1] See *J. Soc. Chem. Ind.*, 1906, 1219 ; 1908, 1214 ; 1909, 1314 ; 1910, 152 ; *Bull. Soc. Ind. Mulhouse*, 1895, 78 ; 1897, 95 ; *Pharm. J.*, **63**, 100.

[2] *Zeitsch. physikal. Chem.*, 1902, **41**, 483.

[3] *J. Chem. Soc.*, 1911, **99**, 1049.

of technical production, in which the production of materials of the same degree of purity is less readily accomplished. The early patent of Phillips on contact sulphuric acid only attained to commercial exploitation when the problem of the removal of arsenical and other "poisons" from the pyrites-burner gases was attained. Volatile silicon compounds act as poisons in the ammonia oxidation process. The presence of minute amounts of sulphur in the iron employed as catalyst for ammonia synthesis is also detrimental to the activity of the catalyst, and traces of sulphur compounds or carbon monoxide in the gases are fatal. Chlorine is to be avoided in the preparations from which the nickel catalyst for hydrogenation and the iron catalyst for the catalytic process of hydrogen manufacture are obtained. Oxides of sulphur and arsenic impair the activity of cuprous chloride in the Deacon chlorine process.

To this imposing list of examples of technical importance a corresponding number from the theoretically interesting catalytic processes might readily be added. The 'sickening' of the Döbereiner platinum by continued use was the object of the early investigations of Turner and Henry, whilst, as previously noted, Faraday devoted considerable attention to the same aspect of the problem in connection with the catalytic activity of his platinum plates. Schönbein[1] pointed out that the hydrides of sulphur, selenium, phosphorus, arsenic, antimony, and tellurium were all active in retarding the reaction between air and hydrogen or ether in the presence of platinum. He was of opinion that the inhibition was due to the formation of a film over the platinum, probably one of solid sulphur or selenium, and not that of a gas film. Bancroft,[2] in a comprehensive memoir on the phenomenon of poisoning, has compiled the following table relative to the effect of minute concentrations of substances as poisons in the decomposition of hydrogen peroxide by means of platinum and by hæmase, the active enzyme of the red blood corpuscles. In the second and third column of the table are given the molar concentrations at which the poisons reduce the rate

[1] *J. pr. Chem.*, 1843, **29**, 238.

[2] *J. Physical Chem.*, 1917, **21**, 767.

Poison.	Colloidal platinum.	Hæmase.
H_2S	M/300,000	M/1,000,000
HCN	M/20,000,000	M/1,000,000
$HgCl_2$	M/2,000,000	M/2,000,000
$HgBr_2$	—	M/300,000
$Hg(CN)_2$	M/200,000	M/300,000
I_2 in KI	M/5,000,000	M/50,000
$NH_2 \cdot OH \cdot HCl$	M/25,000	M/80,000
$C_6H_5NH \cdot NH_2$	—	M/20,000
$C_6H_5 \cdot NH_2$	M/5,000	M/400
As_2O_3	M/50	No poisoning at M/2,000
CO	Very poisonous	No poisoning
HCl	M/3,000	M/100,000
NH_4Cl	M/200	M/1,000
HNO_3	No poisoning	M/250,000
H_2SO_4	,,	M/50,000
KNO_3	,,	M/40,000
$KClO_3$	Slight poisoning (?)	M/40,000

of catalytic decomposition of hydrogen peroxide approximately to one-half of the rate in absence of the poison.

In earlier papers Bancroft had developed the view that contact catalysis involves adsorption. From his *résumé* of the literature of poisons he concludes that poisons act by decreasing the adsorption of the reacting substances on the catalyst. The selective action of this latter on the materials with which it is brought into contact determines the behaviour of the catalyst. On the basis of selectivity, it is easy to understand that the same substances should not necessarily poison both platinum and hæmase, nor should they poison them to the same extent. On the other hand, there is no reason why there should not be a certain parallelism in the two cases. Bancroft points out from the researches of Bodenstein[1] on the oxidation of sulphur dioxide with oxygen in presence of platinum, and from the researches of Bodenstein and Ohlmer[2] on the kinetics of the carbon monoxide–oxygen combination in contact with quartz glass, that in the one case the reaction product, sulphur trioxide, decreases the rate at which the reaction proceeds and that in the other case one of the components of the reaction, the carbon monoxide, decreases the reaction velocity. In both cases the result is attributed to the influence of the negative catalyst on the adsorption of one or more of the reacting substances.

The investigations of Meyerhof[3] on the 'narcotic' action

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[1] *Zeitsch. Elektrochem.*, 1903, **9**, 696.

[2] *Zeitsch. physikal. Chem.*, 1905, **53**, 166.

[3] *Pflüger's Archiv*, 1914, **157**, 307.

of alcohols and urethanes in the catalytic decomposition of hydrogen peroxide by platinum may also be cited in reference to the adsorption view. Ultramicroscopic evidence showed that the addition of the narcotics did not cause an agglomeration of the colloidal particles, and therefore the decreased rate of decomposition is not attributable to such cause. Meyerhof considers it probable that a surface film of the poison is formed over the catalytic agent, which prevents contact of the reacting substances with the catalyst. The retardation caused by alcohols and urethanes in the action of invertase on sugar is also attributed by Meyerhof[1] to displacement of the sugar from the surface of the colloidal invertase. Cases of agglomeration of colloidal particles are, however, not unknown, as was pointed out by Bredig.[2]

It must be emphasised, in view of the multiplicity of cases of catalytic poisoning, that an attempt to find one general explanation for a whole class of phenomena is bound to yield unsatisfactory results. It is certain that in several cases the poisoning is due to direct chemical interaction between the contact substance and the poison, the deterioration of activity being progressive and accumulative. This is true in the case of the poisoning by sulphur gases of a number of metal and oxide catalysts. Further, poisoning in all cases is not directly attributable to the actual ingredient in the gaseous mixture ordinarily designated as the poison. Thus in the case of carbon monoxide in the ammonia synthesis it is probable that, under the experimental conditions prevailing, the carbon monoxide is rapidly and quantitatively converted to methane, which would be found in the exit gases. In such a case the poisoning would be attributable to the action of the water vapour produced during the formation of methane, a viewpoint which would explain also the rigorous necessity of excluding oxygen and traces of water vapour from the reacting gases. Investigation alone will establish in each individual case the laws which govern and determine the retardation observed.

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[1] *Pflüger's Archiv*, 1914, **157**, 251. [2] *Zeitsch. physikal. Chem.*, 1899, **31**, 332.

THEORIES OF CATALYSIS

"There is probably no kind of chemical reaction which cannot be influenced catalytically and there is no substance, element or compound which cannot act as a catalyser."—W. Ostwald.

The phenomena of catalytic acceleration or retardation of physical or chemical processes are so common as to defy systematic classification, since such a complete system would necessarily include all possible types of reactions, both homogeneous and heterogeneous. Thus far we have as yet obtained no accurate information as to the actual mechanism by which chemical reactions proceed, nor are we in a position to apply criteria to distinguish between truly chemical processes in which definite stoichiometric relationships always obtain and that great class of reactions generally described as physical processes such as solution and absorption. These latter are characterised by extreme variability in the 'combining' ratios of the reactants and by the indefinite results yielded by an analysis of the reaction velocities.

Endeavour has been made to express our conception of catalytic activity in the more common terms to which we have become accustomed by frequent use; yet it must not be forgotten that, in the ultimate analysis, such expressions as "compound formation," or "absorption," are similarly deficient in giving us a concept of the reality or nature of the chemical or electrical forces which play a great part in bestowing such unique properties on material substances.

The various alternative theories which have been put forward from time to time to explain the mechanism of this or that catalytic process in influencing the velocity of chemical change may be briefly enumerated as follows :—

(*a*) The formation of intermediate compounds, including the associative theory of chemical combination.
(*b*) The effects of surface a~~b~~dsorption.
(*c*) The electrochemical theory.
(*d*) The effects of an alteration in the density of the absorbable radiant energy.

The theory of the intermediate compound.—In many cases oxidation or reduction of the reagent employed to assist the process occurs. When the reaction is complete the catalytic agent is regenerated by suitable means. As examples may be cited the regeneration of manganese dioxide in the Weldon chlorine process, of bichromates in the oxidation of anthracene to anthraquinone, and of hyposulphites in the reduction of various dyes, such as indigo, to their leuco-bases. The oxidising or reducing agent is thus an oxygen- or hydrogen-carrier and undergoes a complete cycle between the two states of oxidation.

The concept of cyclic action has been applied to the influence of catalysts in both homogeneous and heterogeneous systems.[1] Thus in the Weldon chlorine process the manganese salts undoubtedly function as a catalyst, but owing to the necessity for employing air as an oxidising agent (see p. 104) the oxidation of hydrochloric acid has to be performed in two stages, thus permitting an easy observation of the mechanism of the process. Slightly more complicated, yet capable of experimental proof, are those cases of one-stage oxidation processes in which the catalytic activity of the addition agent may be shown to be due to the oscillation of the catalyst between two states of oxidation. Thus, in the oxidation of anthracene to anthraquinone by means of air in the presence of chromic acid or cerium salts, the presence of both CrO_4'' and CrO_4' ions or cerous and ceric salts may easily be demonstrated, whilst conclusive evidence is forthcoming from the fact that practically complete conversion of the catalyst to the higher state of oxidation may be effected by reducing the quantity of anthracene in solution, whilst reduction may be accomplished by diminishing the air supply.

In many cases, both stages in the cyclic action cannot be isolated, such as in the decomposition of potassium chlorate in the presence of manganese dioxide or in the action of cobalt salts on solutions of bleaching powder.

Again, in the oxidation of aniline to aniline black, where copper salts are employed as catalytic agents, the oscillation between the cuprous and cupric states cannot be observed, yet such an oscillation may be expected to exist. In the

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[1] See Clément and Désormes, *Ann. Chim.*, 1806, 59, 329.

electrolytic preparation of magnesium the presence of a small quantity of ferric chloride is sufficient to lower considerably the electrical efficiency, owing to the alternate anodic oxidation and cathodic reduction of the iron

$$\oplus + \mathrm{Fe}^{\cdot\cdot} \rightleftarrows \mathrm{Fe}^{\cdot\cdot\cdot}$$

a marked case of "carrier" action. In the fractional combustion of methyl alcohol to formadehyde by means of air, using copper gauze as catalytic agent, when performed at low temperatures, a careful inspection of the gauze will reveal an ever-changing colour of the surface of the copper, from which one may infer the alternate reduction and oxidation of one of the various oxides of copper CuO, Cu_2O, or Cu_4O. In the oxidation of ammonia in the presence of the oxides of base metals such as iron, bismuth, and cerium, it has been found that the polyvalent metallic oxides form the best promoters and that the addition of several promoters considerably augments the catalytic activity. We may reasonably assume that such activity is due to the greater range of temperature over which at least one of the oxides is unstable or labile. Such instability is doubtless connected with the dissociation pressure of the oxide at the temperature of operation and the relative affinities for oxygen of the substance undergoing oxidation and the lower oxide of the catalyst material.

It may be argued that intermediate compound formation plays a part in catalytic operations, but that the reaction may proceed through the intervention of some other mechanism. Thus in the preparation of sulphuric acid by the oxidation of sulphur dioxide in the presence of the oxides of nitrogen, nitrosyl-sulphuric acid has been isolated as an intermediate compound, yet evidence is not lacking to show that oxidation can proceed without its formation. It is, of course, quite plausible, in order to combat this argument, to admit the possibility of the formation of some other intermediate compound more unstable and consequently not so easily isolated.

It must be admitted even by the opponents of the theory that the intermediate compound must be labile or unstable for the catalyst to exert a great activity. This point is most frequently urged when oxidation processes using platinum or palladium, and reduction processes, utilising nickel or the former metals, are used as catalytic agents.

Sabatier,[1] as a result of many years' investigations on the use of nickel as a catalyst in hydrogenation processes, came to the conclusion that the formation of an unstable nickel hydride was the hypothesis to which least objection could be raised as an explanation for its extraordinary activity in this respect. Brodie[2] suggested in the case of platinum that an alternate oxidation and reduction of the metal took place in catalytic oxidation processes when this metal was employed. De la Rive[3] inferred that PtO was the composition of the intermediate oxide, which inference was supported by the analytical results of Engler and Wöhler,[4] and of Wöhler.[5] Platinum monoxide, however, even when freshly prepared, is not so active as platinum black, an observation which led these investigators to assume the formation of still higher oxides of platinum, namely, PtO_2, during processes of catalytic oxidation. Bredig, from his researches on the catalytic activity of colloidal platinosols, also came to the conclusion that a definite oxide of platinum was formed.[6]

Examples of various organic catalytic processes supporting the theory of the intermediate compound are by no means infrequent. In the historic example of the preparation of ether from alcohol by means of sulphuric acid, although both Mitscherlich, Berzelius, and Graham recognised the catalytic function of the sulphuric acid, it remained for Williamson[7] to point out that the reaction proceeded through the intermediary formation of sulphovinic acid.

The careful observations of Steele (p. 320) on the use of the chlorides of aluminium and iron in the Friedel-Crafts reaction, led to the isolation of definite chemical compounds, not only between the acylchlorides such as $(C_6H_5{\cdot}CH_2{\cdot}Cl{\cdot}Al{\cdot}Cl_3)_2$, but also between aluminium chloride and the aromatic hydrocarbons themselves. The preparation of the Grignard reagent in which ether is used as catalytic agent revealed

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[1] "La Catalyse en Chimie Organique."

[2] *Phil. Trans.*, 1862, **151**, 855.

[3] *Pogg. Ann.*, 1839, **46**, 489.

[4] *Zeitsch. anorg. Chem.*, 1901, **29**, 1.

[5] *Ber.*, 1903, **584**, 3475.

[6] See also Spear, *Diss. Heidelberg*, 1917.

[7] Brit. Assoc. meeting, Edinburgh, 1850.

the presence of unstable oxonium compounds (p. 314), which can be isolated when special precautions are taken, whilst in the study of enzyme action one is forced to conclude from the characteristic selective action of such catalytic agents that compound formation of definite chemical composition must play an important part in such processes.

On the vexed question of the mechanism of the catalytic operations in hydrolysis, saponification, and ester catalysis, various investigators are ardent supporters of the intermediate compound theory. Thus Bigelow and Kendall (see p. 259) maintain that on addition of hydrochloric acid to, say, an aqueous solution of methyl acetate, complexes are formed between all the reactants thus:

$$\mathrm{HCl{\cdot}(H_2O)_n{\cdot}}\;;\;\;\mathrm{(CH_3{\cdot}CO{\cdot}OCH_3)(HCl)_m}\;;$$
$$\mathrm{(CH_3{\cdot}CO{\cdot}OH)(HCl)_p}\;;\;\;\mathrm{(CH_3{\cdot}OH)(HCl)_q}\;;$$

whilst similar complexes are assumed to exist between the reactants and the ions of the dissociated acid. By utilising strong solutions, thus depressing the hydrolysis of the complex, Kendall has been successful in isolating some of the double salts, and in all cases he has shown that the tendency to double-salt formation is parallel in magnitude to the rate of hydrolysis of the ester when various esters are submitted to hydrolysis with one acid. Similar relationships have been obtained when various acids are used as catalytic agents for hydrolysis of the same ester. Kastle, Acree,[1] and others, on the other hand, assume addition products are formed between the ester and ion only, a point which will be discussed in a subsequent section.

Various modifications of the intermediate compound theory have been suggested, of which the one proposed by H. E. Armstrong is extremely interesting.[2] According to this investigator, chemical combination is reversed electrolysis, and the function of the catalyst is to form a circuit containing at least three distinct terms or components analogous to a closed voltaic circuit. In this way the catalytic agent collects into one system the various elements necessary for a particular

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[1] *Amer. Chem. J.*, 1907, **38**, 489; 1908, **39**, 300.

[2] *Brit. Assoc. Reports*, 1885, 962; *Ency. Brit.*, 1902, **26**, 740.

chemical change, and may be said to form molecular complexes with the reactants. The theory offers a ready explanation of the series of interesting results obtained by Bergmann (1780), Mrs. Fulhame (1794), Dixon (1880), and especially by H. B. Baker,[1] on the influence of small quantities of water on the rate of combination of gases such as hydrogen or carbon monoxide and oxygen. A mixture of dry hydrogen and oxygen, hydrogen chloride and ammonia, or sodium and hydrogen chloride, for example, may be heated nearly to redness (safely to the m.p. of silver) without combination. Combination occurs readily in the presence of conducting water owing to the formation of the voltaic circuit,

$$H_2/\text{Electrolyte}/O_2$$

Baker has noted, however, that "electrolytic" water prepared by the slow union of hydrogen and oxygen does not serve as an active catalytic agent, which fact, according to Armstrong's theory, is easily explicable when the low conductivity of such water is taken into account.

In the bromination of benzene, using ferric chloride as catalytic agent, Armstrong assumes that the ferric chloride combines with both reactants to bring them within each other's range in an unstable system,

$$Br_2/FeCl_3/C_6H_6.$$

Yet another conception of the function of the intermediate compound formed in catalytic operations may be deduced from Liveing's view of chemical reaction.[2]

Liveing cites as example (p. 76) the mutual decomposition of silver oxide and hydrogen peroxide. He points out that the decomposition of hydrogen peroxide is attended with a considerable evolution of heat, and although, when this heat is dissipated through the whole of the liquid, which has a high specific heat, the temperature of the whole is not raised to the point at which silver oxide is decomposed, yet, and this is the fundamental assumption in Liveing's interpretation of chemical changes, the energy liberated by the decomposing

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[1] *J. Chem. Soc.*, 1902, **81**, 400.

[2] "Chemical Equilibrium the result of the Conservation of Energy," London, 1885.

molecules of hydrogen peroxide will be communicated most rapidly and at the highest potential to the molecules of silver oxide with which they are in contact.

It is evident that this view has an important application to those cases where one independent side reaction influences the velocity of, or actually induces the operation of, another reaction. These cases are very frequent in processes of autoxidation and induced reactions (see p. 138) which are not strictly catalytic in action, since the reaction velocity is influenced by a secondary reaction and not by a catalytic agent. It is evident, however, that the idea may be extended to catalytic operations. Thus, we may regard the function of platinum in the combination of oxygen and hydrogen as not strictly catalytic, the slow conversion of platinum into platinum oxide being attended by the liberation of energy sufficient to accelerate the combination of the neighbouring molecules of hydrogen and oxygen, or, on the other hand, we may regard it as periodic and truly catalytic.

Thus, the formation of platinum oxide can be assumed to be attended with the liberation of sufficient energy to effect the combination of the neighbouring molecules of hydrogen and oxygen. The exothermicity of this reaction is, however, extremely great, and, assuming Liveing's hypothesis of local energy transfer, we may assume that the platinum oxide is again decomposed into metallic platinum and oxygen. The surrounding medium then cools down and the process starts *de novo*. The catalyst is thus an energy conveyer through the intermediate formation of an unstable compound. It may, of course, be justly argued why, when one molecule of oxygen has reacted with two of hydrogen, this combination should not serve as a focus of an explosion or of an ever-extending zone of slow combustion. Against this argument it may be urged that the energy of combination of the few molecules in the free gas space is dissipated with extreme rapidity in the homogeneous gas mixture, and no other molecules receive sufficient of the energy dissipated to raise their internal energy to that required for reaction, whilst at the surface of the metallic platinum a localisation of the dissipated energy occurs permitting the operation of the cycle alluded to above.

Several cases of periodic chemical action will be referred to in the subsequent pages of this work which are certainly capable of interpretation on Liveing's hypothesis of the localised dissipation of energy.

From these few observations it will be noted that the conception of the intermediate compound offers a simple interpretation for many catalytic processes, and it may be said to offer an intelligible solution for the *modus operandi* of the majority of such reactions.

The adsorption theory of catalysis.—As a result of Döbereiner's investigations on the catalytic activity of platinum black in accelerating the combustion of hydrogen and oxygen,[1] De la Rive[2] developed the theory of the intermediate compound in which platinous oxide played the part of oxygen carrier to the hydrogen. Berthelot's suggestion,[3] that a hydride of platinum carried hydrogen to the oxygen, never received much support.

M. Faraday,[4] on the other hand, as a result of a series of experiments on electrolytic gas, rejected the compound theory and advanced the hypothesis that the catalytic activity of platinum in accelerating the combination of hydrogen and oxygen was due to the adsorption of both hydrogen and oxygen on the surface of the metal in the form of a compound film.

He writes as follows[5]: "Hence it would seem to result that the particles of hydrogen or any other gas or vapour which are next to the platina, etc., must be in such contact with it as if they were in the liquid state, and therefore almost infinitely closer to it than they are to each other, even though the metal be supposed to exert no attractive influence over them." Faraday argued that the reaction velocity should be considerably augmented in this compressed film, not only because the number of molecular impacts per unit of time would be considerably augmented by such compression,—"the particles are in the most favourable state possible for combination upon the supervention of any determining cause,

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[1] *Ann. Chim.*, 1823, **24**, 93.

[2] *Pogg. Ann.*, 1834, **46**, 189.

[3] *Compt. rend.*, 1882, **94**, 1377.

[4] "On the Power of Metals and other Solids to Induce the Combination of Gaseous Bodies," Nov. 30th, 1833.

[5] P. 63.

such as either the negative action of the platinum in suppressing or annihilating as it were their elasticity on its side" —but also because in the act of absorption those forces which prevent combination would be decreased, an important consideration which has only recently been the subject of systematic investigation and which will be referred to later.

Faraday also laid the foundations of the most interesting and important generalisation of the adsorption theory by his studies on the combination of hydrogen and oxygen in the presence of carbon monoxide. In the presence of this gas, hydrogen and oxygen would not undergo combination at the surface of cold platinum, and similar results were obtained with olefiant gas and ether; the platinum, however, had not undergone any permanent change, as was found to be the case on the addition of phosphine or arsine to the gas mixture, since it re-exerted its normal activity on a fresh gas mixture. Faraday himself had no definite opinion as to the cause of these phenomena. He says:

"Whether the effect produced by such small quantities of certain gases depends upon any direct action which they may exert upon the particles of oxygen and hydrogen by which the latter are rendered less inclined to combine, or whether it depends upon their modifying the action of the plate temporarily (for they produce no real change on it) by investing it through the agency of a stronger attraction than that of the hydrogen, or otherwise, remains to be decided by more extended experiments."

The earlier investigations on the fractional combustion of gases by Henry,[1] Turner,[2] and others, indicated that Faraday's speculation on the possibility of selective absorption was in all probability the correct one. In §(353) Faraday remarks: "In fact, the very power which causes the combination of oxygen and hydrogen is competent, under the usual casual exposure of platina, to condense extraneous matters upon its surface, which, soiling it, take away for the time its power of combining oxygen and hydrogen, by preventing their contact with it."

Faraday's concept of catalytic activity being due to adsorp-

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[1] *Ann. of Philosophy*, 1825, **25**, 422.

[2] *Edin. Phil. J.*, 1824, **11**, 99, 311.

tion phenomena has been advanced from a slightly different point of view by Sir J. J. Thomson,[1] who has shown, as a logical deduction from Laplace's theory of capillarity, that in chemical combination between thin layers of liquid there is a factor present which is absent in the case of liquids in bulk, and we may expect that chemical combination between the layers of liquids might take place even though it were absent in ordinary cases. Some idea of the process imagined may be gathered from the following considerations.

According to Laplace, the attractive force between two molecules of a liquid is a function of their distance apart (Fig. 2), z, from the point of contact up to the range of molecular action.

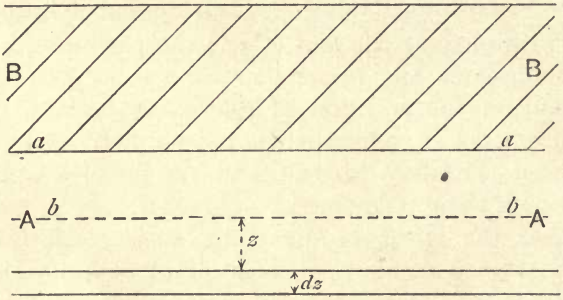

FIG. 2.

If we imagine two fluids A and B of densities σ_1 σ_2, separated by a boundary surface $a-a$, we can easily calculate the expenditure of work required to produce unit area of interface between A and B on the boundary surface a, a. Considering in one fluid, A, the presence of a boundary surface, b, b, we can find the attractive force between a thin lamina of fluid δz in thickness and the homogeneous boundary surface, b, b, if it be a distance z from this surface.

The force on unit area of the layer is equal to $\sigma_1\phi(z)\sigma_1\delta z$. Hence the mutual pull of the liquid on each side of the boundary surface per unit area is equal to

$$\sigma_1{}^2\int_0^\infty \phi(z)\,dz,$$

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[1] "Applications of Dynamics to Physics and Chemistry."

and the work required to remove any slice δz in thickness at a distance z from the boundary surface is

$$\sigma_1{}^2\,\delta z\int_z^\infty \phi(z)\,\delta z.$$

Consequently, the work required to form a new common surface in A of unit area is

$$\sigma_1{}^2\int_0^\infty\int_z^\infty \phi(z)dzdz = \sigma_1{}^2 z\int_z^\infty \phi(z)dz - \sigma_1{}^2\int_0^\infty z[-\phi(z)]dz.$$

$$= \sigma_1{}^2\int_0^\infty z\phi(z)dz,$$

since the first term vanishes at both limits.

Since two new surfaces are formed in this way, one on each side of b, b, the work required to form unit surface is

$$\tfrac{1}{2}\,\sigma_1{}^2\int_0^\infty z\phi(z)dz.$$

In a similar manner, the work required to form unit surface in B is

$$\tfrac{1}{2}\,\sigma_2{}^2\int^\infty z\phi(z)dz.$$

Whilst the work done in allowing a unit surface of A to come into contact with a unit surface of B under their own molecular forces is

$$\sigma_1\,\sigma_2\int_0^\infty z\phi(z)\,dz.$$

Hence the total expenditure of work required to produce a surface of unit area at the interface of A and B is

$$\tfrac{1}{2}\left\{(\sigma_1{}^2+\sigma_2{}^2)-2\sigma_1\,\sigma_2\right\}\int_0^\infty z\phi(z)dz$$

$$=\tfrac{1}{2}(\sigma_1-\sigma_2)^2\,C,$$

where C is a constant for all surfaces,

$$=T_{AB},$$

where T is the interfacial surface tension.

Let us assume that in between A and B there is formed a third fluid layer, C (Fig. 3), of density the mean between A and B. Then since

$$\sigma_3 = \frac{\sigma_1 + \sigma_2}{2}$$

$$\sqrt{T_{AB}} = \sqrt{T_{AC}} + \sqrt{T_{CB}}$$

$$\text{and } T_{AC} = T_{CB}$$

$$\text{or } T_{AC} + T_{CB} = \tfrac{1}{4}T_{AB}\,.$$

Hence the energy of each area is only one-quarter of the energy of the original area, and the total energy due to the surface tension only one-half what it was before; by interposing n films between A and B, the energy is reduced to $1/_{n+1}$ of its original value. It is therefore evident that combination between A and B would decrease the energy due to surface tension. Thus, under these conditions, capillarity will tend to increase the chemical action.

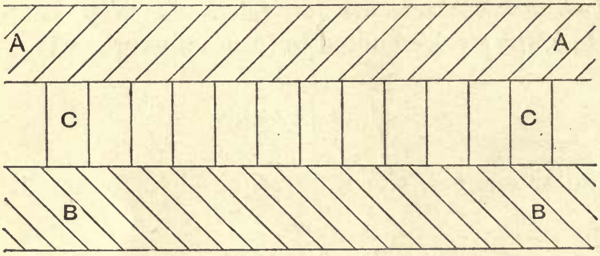

FIG. 3.

Many cases are known in which such surface tension phenomena affect both the rate and the final equilibrium of a reacting system. In plant cells the large amount of surface energy available from a slight alteration in the surface tension frequently outweighs any thermal energy which may result from chemical action.

Sir J. J. Thomson has noted several anomalous reactions with dyestuffs when caused to react in thin films and similar observations have been made by Liebreich,[1] Liveing,[2] Bredig,[3] and others.

Bancroft,[4] in a series of recent communications, has care-

[1] *Phil. Mag.*, 1887, **23**, 468; 1890, **29**, 216.

[2] *Proc. Camb. Phil. Soc.*, 1883, **14**, 370.

[3] *Zeitsch. physikal. Chem.*, 1899, **31**, 258.

[4] *J. Physical Chem.*, 1917, **21**, No. 8.

fully reviewed the whole subject of selective combustion of gases in the presence of solid catalytic material and has come to the conclusion that the facts are capable of the simplest explanation on the adsorption hypothesis.

He points out that from the work of Turner, Henry, Lunge and Harbeck,[1] Bone,[2] and others, the order of preference of adsorption, as judged by the criterion of selective combustion, may be varied by change of adsorber or solid contact material, and gives the following orders :—

Catalytic material.	Order of preference in adsorption.
Platinum	CO, H_2, C_2H_2, CH_4
Charcoal	C_2H_2, H_2
Borosilicate glass	CH_4, H_2

The writers have observed the following interesting sequence, using oxide of iron as catalytic material H_2S, S, CO, H_2.

Restriction of the catalytic activity may likewise be brought about by the selective adsorption of a poison such as grease or carbon monoxide in the case of platinum or of a product of the reaction, such as carbon dioxide, in the combustion of carbon monoxide or of sulphur trioxide in the contact process for the manufacture of sulphuric acid. Bancroft, furthermore, points out that stabilisers added to colloidal catalysts may cut down their catalytic activity owing to a decrease in their adsorptive powers, but this factor may be partially compensated for by an increase in the surface of contact.

In addition to the general statement that selective adsorption permits of different reactions being accomplished with the aid of different catalytic material, Bancroft lays emphasis on two important points. First, catalysts tend to produce the system which they adsorb most strongly, and secondly, the compound or adsorptive layer may be regarded as a solvent and hence may exert an influence on the final equilibrium, a point which we have seen has been fully developed by Sir J. J. Thomson on the theory of capillarity. It is evident, on either the hypothesis of the intermediate compound or the theory of selective adsorption, that the presence of a relatively large quantity of catalyst cannot fail to influence the equilibrium value of the reacting constituents since they may be nearly entirely withdrawn from their normal conditions

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[1] *Zeitsch. anorg. Chem.*, 1898, **16**, 50.

[2] *J. Chem. Soc.*, 1902, **81**, 538.

of reaction to form an intermediate compound with the catalyst or pass into the adsorbed layer, where they may re-establish equilibrium different from that which would occur in their normal state.

On the other hand, however, a catalyst even when acting as a new medium cannot influence the equilibrium when the reactants are removed from the sphere of influence of the catalyst, otherwise the possibility of a *perpetuum mobile* would present itself. The following example, however, will serve to emphasise the point.

If a mixture of nitrogen and hydrogen in the stoichiometric ratio of one to three be passed through a layer of granulated iron-molybdenum at a temperature of 500°, the two gases will be compressed on the catalyst surface, there to react to form ammonia in the equilibrium amount dependent on the pressure obtaining in the adsorbed layer. The gaseous mixture passing from the adsorbed layer being displaced by fresh gas, undergoes decomposition as it passes through the areas of decreasing pressure and emerges into the gas stream with the equilibrium amount obtaining at that pressure and temperature. It is evident that at the adsorbing surface itself, where the gas pressure is a maximum, the conversion to ammonia must be in excess of that demanded by conditions in the normal gas stream, and furthermore, since the product of the reaction is selectively adsorbed, the actual concentration of ammonia must be extremely high.

This point opens out a vista of interesting speculation as to whether mechanical energy cannot be converted into chemical energy by such a process. If ammonia is selectively adsorbed at the catalyst surface, it may be possible to drive off this gas by expenditure of work, conveniently by forcing fresh gas to the surface, without its subsequent decomposition to the normal uncompressed equilibrium values. Concentrations of ammonia would thus be obtained in the normal gas stream in excess of that demanded by the equilibrium values for that particular temperature and pressure at the expense of mechanical energy expended in renewing the adsorbed gas films.

According to Jellinek,[1] indications of the presence of am-

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[1] *Zeitsch. anorg. Chem.*, 1911, **71**, 121.

monia in excess of the normal equilibrium amount have already been obtained. It would be of the greatest interest to obtain confirmation of these results.

Characteristics of the adsorption layer.—Various estimates have been given for the thickness of the absorbed layer of gases or liquids on a solid surface. The magnitude naturally varies with the nature of the adsorbing surface and the material in contact with it. The quantity adsorbed is likewise dependent on the concentration of the substance in the surrounding medium, and is inversely proportional to the absolute temperature as indicated by W. Gibbs's equation :—

$$\Gamma = - \frac{c}{RT}\frac{\delta s}{\delta c},$$

where c is the concentration of the solute adsorbed in the surrounding medium, Γ the "adsorption coefficient" or the mass of solute per sq. cm. less the amount which would originally have been present if no adsorption had taken place, and s the interfacial surface tension. In the following table are summarised the approximate values found for such adsorption film thicknesses and also the average distance between the molecules in gases and liquids at N.T.P.

Range in $\mu\mu$ *	Measurement.	Observer.
0·02	Inferior limit to diameter of gaseous molecules.	Kelvin.
0·07—0·02	Mean distance between centres of liquid molecules.	,,
0·011—0·014	Diameter of gaseous hydrogen molecule.	O. Meyer, Exner, Van der Waal.
3—4	Mean distances between centres of gaseous molecules.	O. Meyer.
1	Thickness of electric double layer.	Lippmann and Oberbeck.
1—3	Thickness of metal films which polarise platinum.	Oberbeck.
12	Thickness of silver plate affecting the phase of reflected light.	Wiener.
12	Thickness of black soap film.	Rücker and Reinold.
50	Thickness of normal film.	Quincke.
96—45	,, ,, ,,	Rücker and Reinold.
118	Superior film thickness in soap.	Plateau and Maxwell.
1350	,, ,, ,,	Rücker and Reinold.
10.5	Thickness of permanent film on glass at 21°.	Bunsen.
500	Thickness of adsorbed CO_2 film on charcoal.	Mitscherlich.

* 1 $\mu\mu = 10^{-7}$ cm.

It must be noted, however, that Bakker's more recent determination for the film thickness of CO_2 on charcoal[1] only amounts to 1. Gurvitsch's figures[2] for the thickness of the adsorbed layer on other materials are also of interest :—

Substance.	Thickness of film in $\mu\mu$.	
	Silver foil.	Glass wool.
CCl_4	35	30
CS_2	33	31
$CH_3 \cdot CO \cdot CH_3$	28	26

From the above figures it is evident that the film thicknesses are by no means inconsiderable and that the actual quantities of gas or liquid absorbed per sq. cm. of surface may rise to quite high values. The quantity adsorbed is naturally under a pressure which, where in contact with the solid itself, is probably extremely high. At present no information is forthcoming on the rate at which the pressure falls off with the distance from the surface, since Laplace's function, $F=K\phi(z)$, has not been evaluated.

The internal pressure in liquid water as calculated from the latent heat of evaporation is approximately 10,500 atmospheres, in ethyl ether 1,300, in ethyl alcohol 2,100, and in carbon disulphide 2,900. An alternative method of approximating to a value of the average internal pressure in an absorption layer is obtainable from the magnitude of the electrostriction which would be produced inside an electrical double layer, 10^{-7} cm. thick. If the potential difference were one volt, and assuming the specific inductive capacity had the value of unity, the electrostriction would exert a pressure of 4,400 atmospheres per sq. cm.

The difficulty with which the thin films of moisture are removed from glass apparatus, usually requiring heating to 350° in a high vacuum, shows that the adhesive forces are by no means inconsiderable whilst Mitscherlich[3] has shown that at least one-third of carbon dioxide compressed on charcoal would be in the liquid form as a result of such compression.

We have already noted that gases appear to be selectively adsorbed ; the quantity of the several gases adsorbed per

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[1] *Zeitsch. physikal. Chem.*, 1916, **91**, 571.

[2] *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 805.

[3] *Pogg. Ann.*, 1843, **59**, 94.

sq. cm. of adsorbent or per gram of uniform-sized material is roughly proportional to the compressibility and ease of condensation of the gas, as is shown by the following figures :

	Volume (corrected N.T.P.) per c.c. of charcoal	
Gas.	at 0°,	at −180°.
Helium	2	15
Hydrogen	4	135
Nitrogen	15	155
Oxygen	18	230
Carbon dioxide	500	—

The velocity of adsorption is extremely rapid, equilibrium being usually established in a few seconds.

It will be noted that, since the value of $1/n$ in Freundlich's equation for the reaction isotherm ($K = ap^{1/n}$, where K is the adsorption per gram, a a constant depending on the characteristics of the gas and p the partial pressure of the gas adsorbed) sinks with lowering of temperature whilst the value of a rises, the separation of oxygen and nitrogen from cold air can be brought about by this means. Dewar has found that charcoal adsorbs equal quantities of oxygen and nitrogen from air at −180°.[1]

On the adsorption theory, the function of promoters added to a catalytic material would be to establish, by selective action, the optimum concentration of the reactants on the catalyst surface. Thus at 500°, uranium carbide appears to adsorb both hydrogen and nitrogen in approximately the correct stoichiometric ratios to form ammonia, and is thus the most active catalytic material to use. Other catalysts, such as iron or cobalt at 550° adsorb hydrogen and but little nitrogen, but by the addition of a promoter such as molybdenum or titanium a partial compensation for this deficiency of nitrogen can be obtained. It must not be forgotten, however, that alteration in temperature will effect not only the absolute amounts of the adsorbed constituents, but also their relative amounts. Thus, although it is possible to effect the selective combustion of hydrogen in the presence of methane with limited amounts of oxygen at relatively low temperatures, all traces of any selective action disappear with elevation of the temperature. A more detailed account of the phenomena

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[1] *Proc. Roy. Soc.*, 1904, **74**, 124.

occurring in adsorption processes and the thermodynamical treatment of the subject are to be found in the following text-books, to which the reader is referred :

J. W. Gibbs, " Scientific Papers, I."

H. Freundlich, " Kapillarchemie, 1906."

J. J. Thomson, " Applications of Dynamics to Physics and Chemistry," 1888.

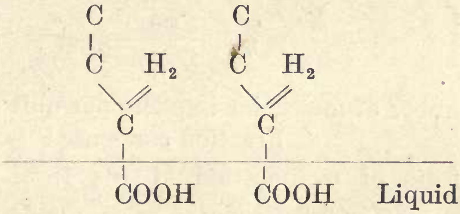
The electrochemical theory of catalysis.—We have noted that whilst the intermediate compound theory offers a ready interpretation of a number of homogeneous catalytic reactions, yet its application to heterogeneous catalysis is somewhat forced, since in many cases we must postulate the existence of unknown compounds, as in the catalytic decomposition of many substances such as AsH_3 or PH_3 on glass surfaces or the oxidation of methane at the surface of borosilicates. The adsorption theory based on the generalisations of Faraday offers a more promising concept of heterogeneous catalysis, but for homogeneous reactions an easy interpretation is not forthcoming.

Faraday himself was of the opinion that in the adsorbed layer not only was the frequency of molecular collision increased, but those forces normally operating to oppose chemical combination were considerably reduced in intensity.

Doubtless the effect of compression on the specific inductive capacity of the medium in the compressed layer considerably augments the velocity of reaction since the value of the specific inductive capacity of a gas is raised by compression ($K_p = K_o(1 + ap - \beta p^2)$, (where $a = 10^{-4}$ approx.) and reactions generally proceed quicker in solvents of high dielectric capacities.

Thus Cavendish showed that the oxidation of nitric oxide proceeded more rapidly in aqueous solution than in the gaseous state. Dixon's observations on the oxidation of sulphur dioxide led to similar conclusions, whilst the partial agreement between reaction velocity and the specific inductive capacity of liquid solvents has been confirmed by numerous observers (see p. 24). Many other observations, however, tend to indicate that this *per se* is not the important factor which Faraday laid stress on. It is extremely probable that in the adsorbed layer there exists an orientation of the molecules.

This hypothesis receives considerable support from the work of Langmuir,[1] Harkins,[2] and Marcelin,[3] on surface tension phenomena. Langmuir has indicated that in thin films of fatty acids floating on water, a definite orientation of each acid molecule to the water seems to exist. Thus, the carboxyl groups are immersed in the water and the hydrocarbon chains are crowded into the gas space above:



A conception of contact action of this kind led Twitchell (see p. 271) to the development of his process for the hydrolysis of the fatty glycerides.

According to Langmuir, the adsorbed film, which is bound to the adsorbing surface by chemical forces, namely, the primary or secondary valencies, should be only one molecule thick. He points out that the relatively "thick" film thickness obtained by various observers is to be accounted for by the fact that porous or capillary spaced bodies are usually employed as adsorbents or that saturated vapours have been utilised for obtaining comparative figures, under which conditions condensation of liquid may take place in the capillary spaces. In some instances, solution and absorption may be mistaken for adsorption.

Langmuir has developed this general theory of adsorption to the particular case of the adsorption of gases by plane solid surfaces, and records the results of a series of experiments on the adsorption of various gases by sheet platinum, glass and mica at low pressures (ca. 0,1mm. mercury) and various temperatures. In the case of glass and mica, the order of the gases in their magnitudes of adsorption was always the same and in the following order: hydrogen, oxygen, argon,

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[1] *J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; 1918, **40**, 1361.

[2] *Ibid*, 1917, **39**, 541.

[3] *Ann. Physik*, 1914, **1**, 19.

nitrogen, carbon monoxide, methane, and carbon dioxide. The adsorption process was shown to be reversible and very slight with these materials at the ordinary temperature, less than 1 per cent. of the surface being covered with a layer one molecule thick. At lower temperatures (– 118° to – 183°) and at higher pressures, saturation could be obtained, the amount adsorbed varying with the pressure according to the relationship

$$\frac{N}{N_0} \times \eta = \frac{\sigma\mu}{1 \div \mu\sigma}$$

where μ = number of molecular impacts per unit area.

$$\sigma = \frac{\text{Fraction condensed}}{\text{Rate of evaporation of gas from an entirely covered surface.}}$$

η = gram-molecules absorbed per unit area.

N = Avogadro's constant.

No adsorption with platinum could be observed until the metal had been activated by heating to 300° in hydrogen and oxygen at low pressures. The metal thus treated would adsorb hydrogen, oxygen, and carbon monoxide, the maximum quantities of the two latter gases corresponding with unimolecular layers. Carbon dioxide showed no tendency to be adsorbed at the ordinary temperature, and it was found that oxidation of hydrogen or carbon monoxide by oxygen could easily be effected at the temperature of the room. The adsorption of carbon monoxide or oxygen is not reversible, and complete removal could not be effected by exhaustion.

Emphasis may also be laid upon the electrochemical measurements of Palmaer, Ostwald, J. J. Thomson, and many others, which indicate the existence at all absorptive boundaries of an electrical double layer. This can only be brought about by electrical orientation of a layer of neutral molecules or, in the case of ionised substances, of selective adsorption of one of the ions of the molecule, resulting in the formation of a layer of the ions of opposite sign held by electrostatic attraction to the surface of the adsorbing medium.

On the hypothesis of directive as well as of selective adsorption the gulf between the intermediate compound and the adsorptive theory is bridged, since the postulate of directive force necessarily assumes some form of chemical union between the contact surface and the molecules of the surrounding medium. These quasi-chemical combinations may, according to this view, become sufficiently definite as to give the complex all the characteristics of a chemical compound.

This theory of catalytic operations can be applied to consideration of the phenomena of enzyme actions.

Thus, from the velocity coefficients of the reaction between an enzyme and a co-enzyme, from the apparent false equilibrium obtained in the Danysz effect in the combination of a toxin and an antitoxin and in the fractional but not stoichiometric removal of an enzyme from the sphere of action in many hydroclastic processes, by the products of the reaction, the evidence for the purely adsorptive nature of such combinations is extremely strong. This view is further supported by the action of small traces of ionising salts on the enzyme activity, which can easily be attributed to selective ion adsorption. On the other hand, the selective nature of the enzyme actions and the fundamental relationships which must exist between an enzyme and its co-enzyme to cause only these two substances to react can only be interpreted on the hypothesis of chemical combination. It seems that the primary action is one of adsorption, and that chemical combination proceeds after the adsorption has completed itself. In this case we can observe the gradual conversion of an adsorptive compound into a real chemical molecule or a gradual strengthening of the bonds of combination.

Attempts have been made to apply this conception to homogeneous systems, and H. E. Armstrong's associative theory (p. 41) is clearly a simple extension of the broad principles of the adsorptive theory.

In the chapter on catalytic operations in organic chemistry many instances will be found in which the process of compound or complex molecule formation may be readily explained and anticipated in new reactions by making certain assumptions as to the electro-positive or electro-negative character of an atom or a radicle. These assumptions, which will be dealt with in that section, are by no means forced or laboured, since they can be logically deduced from the magnitude of the electrolytic potentials of the elements themselves, and although as yet we have no realistic conception of the nature of the forces which govern these magnitudes, they are characteristic and unique properties of the elements. Furthermore, from the physico-chemical investigations in atomic structure during the present century it appears more than likely that we are justified in expressing our magnitudes in terms of electrical pressure instead of in any other intensity factor.

Again, in photo-chemical processes we have instances in which radiation causes the primary combination by the discharge of an electron from one of the molecules. By the subsequent impingement of this discharged electron on other neutral molecules their combination can be effected owing to the enhanced activity of the complex molecule-electron, and combination will only cease when the travelling electron comes into collision with its original positive "rest" and is absorbed by it. Radiation in this case functions as an inductive agent and the electron is the actual catalyst.

In most cases of combustion and in many cases of violent chemical action such as the oxidation of metals or the interaction of alkali and bases, the presence of electrons may be demonstrated; that they are not manifested in all cases of chemical action may be due, not to their absence, but to the fact that in the case of heterogeneous catalysts their kinetic energy when discharged from the inactive molecule is not sufficient to break through the electrical double layer, or adsorption film on the catalytic surface, whilst, in homogeneous reactions, practically immediate recombination with the positive "rest" occurs. Sir J. J. Thomson[1] gives many instances in which the presence of the electron or electron-molecule complex or the positive rest may be demonstrated, when precautions are taken to break down the electrical double layer by mechanical means.

Radiation frequency and catalysis.—It is well known that the reaction velocities of most chemical reactions are influenced by a change in temperature of the reactants. Thus, hydrogen and oxygen can exist at the ordinary temperature without undergoing any apparent reaction. At

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[1] "Conduction of Electricity through Gases."

600°, combination proceeds with such an extreme rapidity that explosion frequently results. The effect of temperature is usually exponential, the velocity constant more than doubling itself for a 10° rise, although the exceptions are sufficiently numerous to define this statement more as a generality than as a rule. Arrhenius[1] pointed out that such a high temperature coefficient could not be deduced from a consideration of the increase in the number of the molecular collisions between the reacting molecules for a 10° rise in temperature. This may be calculated from the kinetic theory. Less than a 2 per cent. increase in the number of molecular impacts is to be expected on this basis.

It must therefore be assumed, either that some other factor is operative in increasing the number of molecular impacts with rise in temperature in addition to an increase in the kinetic energy of the molecules and the decrease in the viscosity of the medium, or, as postulated by Arrhenius, that, at all times, the number of molecular impacts per unit of time is amply sufficient to account for the velocity of chemical change, not all such molecular collisions, however, being effective in producing chemical change. From these considerations, Arrhenius was led to the concept of active and inactive molecules in which the equilibrium between these two tautomeric forms of the same substance shifted in favour of the active form with rise in temperature. This concept was subsequently extended by Arrhenius to explain the mechanism of catalytic influence, the addition of the catalyst being presumed to bring about an increase in the concentration of the active form. The alteration of the velocity coefficient with the temperature could be formulated in the expression,

$$\frac{d \log K}{dT} = \frac{E}{RT^2},$$

E being the energy required to transform one gram-molecule from the inactive to the active state. This mathematical formulation of the influence of temperature has been adopted in most of the subsequent researches on the subject, and its application to the phenomenon of catalytic action has largely been employed. Recent investigation, however, in

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[1] *Zeitsch. physikal. Chem.*, 1889, **4**, 22 ; 1899, **28**, 317.

Arrhenius's laboratory has brought forward evidence in apparent disagreement with the concept of an equilibrium between active and inactive molecules.[1]

Marcelin[2] deduced a similar expression to that of Arrhenius, on the assumption that an inactive molecule becomes active when its internal energy exceeds a definite critical value, E, in the above equation, becomes, in Marcelin's expression, the extra amount of energy or critical increment of energy[3] in excess of the average energy of the molecules which has to be supplied to effect this conversion. Lewis[4] has applied Marcelin's concept of conversion of inactive to active molecules by a critical energy increment to homogeneous catalytic processes, utilising a mathematical formulation of the concept developed by Rice and having the form

$$\frac{d \log K}{dT} = \frac{V_c - V_m + \frac{1}{2} RT}{RT^2},$$

where V_c denotes the critical value of the internal energy of a number of the molecules, and V_m the mean potential energy of the molecules. According to Rice, when a positive catalytic effect is present, a negative term is introduced into the numerator, thereby lowering its value to an increasing degree with increasing concentration of the catalyst. Lewis cites experimental evidence in support of such a view. From an examination of the literature, Lewis also concludes that the larger the velocity constant of a reaction the smaller is the value of the numerator in the above equation. The source of energy increment is to be found in the infra-red radiation of the system, and preliminary measurements of the infra-red absorption spectra of hydrogen chloride, potassium chloride, and methyl acetate in aqueous solution were carried out in order to sustain this point of view in regard to catalytic action in the hydrolysis of esters by acids in presence of neutral salts.

The elementary treatment of the problem given by Lewis[5]

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[1] See Taylor, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, 2, No. 34.

[2] *Compt. rend.*, 1914, **158**, 161.

[3] Lamble and Lewis, *J. Chem. Soc.*, 1914, **105**, 2330.

[4] *Idem*, 1914, **105**, 2330; 1915, **107**, 233; 1916, **109**, 55, 67; 1917, **111**, 389, 457, 1086; 1918, **113**, 471.

[5] *Rep. Brit. Assoc.*, 1915, 394.

is amplified in the later papers of the series cited above. It is shown that quantitative expressions for the velocity, temperature-coefficient, and effect of the catalyst can be developed from the radiation hypothesis, infra-red radiation being absorbed in terms of quanta. The expressions derived are all in agreement, over limited ranges of temperature, with the empirical equation of Arrhenius, the general applicability of which is well known. Further, it may be deduced on these grounds that the addition of a negative catalyst raises the temperature-coefficient whilst a positive catalyst diminishes it. The further development of the radiation hypothesis has been directed towards the elucidation of the problem of general chemical reactivity, rather than in connection with catalysis which is regarded as a special case of chemical reactivity. The heat of reaction, the equilibrium constant, and the absolute velocity constants of gas reactions have all been investigated by Lewis from the point of view of radiation, the material accumulated being necessary to the eventual investigation of catalytic processes in particular.

A consideration of the preceding theories, however, serves to show that the reactivity of a molecule may undergo exaltation without a rise in the energy of the molecule occurring. Successful combination as a result of molecular collision is certainly stimulated by an increase in the energy of the impinging molecules, but, at the same time, similar results appear to be capable of attainment by directive collision in which the reactive parts of each molecule are brought into juxtaposition by some suitable artifice of molecular orientation. Especially does this seem to be possible in the case of heterogeneous catalysis, with which, however, Lewis has thus far not dealt.

CHAPTER III

THE MEASUREMENT OF REACTION VELOCITY IN CATALYTIC PROCESSES

THE development of the science, as well as the technical application of catalytic processes, has been based upon numerous isolated observations of the influence which certain substances exert on the reaction velocity of many homogeneous and heterogeneous chemical reactions. During the last thirty years the quantitative aspect of the problem has received an ever-increasing attention and the measurement of the influence of known quantities of catalytic substances on the reaction velocity, under certain fixed conditions of temperature and pressure, is fundamental to the subject.

In homogeneous reactions the problem is one of comparative simplicity, since the course of the reaction may be followed by any of the suitable chemical or physical methods, such as the liberation of gases, *e.g.*, in the decomposition of hydrogen peroxide, hypochlorites, or diazoacetic esters; by chemical titration, as in ester hydrolysis or the liberation of iodine; by electrical conductivity, utilised by Hantzsch in his studies on the conversion of pseudo-acids, or by change in optical rotatory power, as in sugar hydrolysis. Other methods based upon the measurement of the rate of change of the electrolytic potential of an electrode in a known solution, or of an irreversible electrode in a changing electrolyte, or again of colour, diathermicity, or dilatation of solutions or gaseous mixtures are occasionally employed. The relative concentrations, if a solvent be employed, are given in grams per litre, owing to the frequent uncertainty as to the state of molecular complexity of solutes in various solvents.

The measurement of reaction velocity as a function of catalytic activity in heterogeneous systems is, however, by no means such a simple operation, since various factors, absent in homogeneous reactions, become operative and have to be taken into consideration when the quantitative aspect of the problem is under investigation.

Investigations on heterogeneous catalytic processes may for this purpose be broadly classified into two groups :

(*a*) Those in which the reactants proceed to equilibrium in the presence of a definite amount of catalytic substance.
(*b*) Those in which the reactants are passed through the catalytic material under given conditions and are subsequently collected and submitted to analysis.

In those cases in which a predetermined quantity of a mixture of the reactants is permitted to react in the presence of a definite amount of catalytic substance two important factors have to receive attention ; first, the measurement of the reaction velocity as a function of the quantity of catalytic material ; and, secondly, the dispersivity of the heterogeneous catalyst in the homogeneous medium.

We have already noted that in homogeneous reactions the reaction velocity is generally proportional to the concentration of the catalyst, *i.e.*,

$$K = f(m),$$

where f is the proportionality factor.

In heterogeneous reactions, such as the decomposition of arsine or hydrogen iodide on glass surfaces, or the liberation of oxygen from hydrogen peroxide in the presence of colloidal metals, or the various clastic processes of enzyme actions, the reaction velocity is influenced rather by the active volume of catalytic material ; thus, in decompositions taking place on glass or metal surfaces K is roughly proportional to the area of the catalytic surface.

$$K = f(A).$$

The investigations of Bodenstein on the kinetics of gas reactions in glass and quartz vessels have contributed greatly to our knowledge of such surface action.[1]

[1] *Zeitsch. physikal. Chem.*, 1903, 1904, 1905, 1907.

In other cases, where the heterogeneous catalyst is a colloid, the mass of the added catalytic material is usually determined.

Only as a first approximation may one consider that the mass of, say, a given quantity of platinum in a platinosol is proportional to the active volume, since the active volume is practically confined to a surface skin of no very considerable thickness.

There exists, of course, a considerable amount of uncertainty as to how far the density of the metal itself is altered during sol formation, and, again, how far the sol particles may be regarded as smooth- or rough-surfaced spheres or ellipsoids.

An approximation to the surface of a colloidal sol may be obtained by an estimation of the number of sol particles per c.c. or the volume concentration (n), and by a determination of the mean radius of each particle (r). The mean area of catalyst surface per c.c. of substrate (or the gram concentration) is then given by :

$$A = 4\pi r^2 n$$

and the mass M by $\frac{4}{3}\pi r^3 \rho n$
(ρ being the density of the metal.)

Hence

$$\frac{A}{M} = \frac{3}{\rho r},$$

or, a factor proportional to the active volume or surface area per c.c. may be obtained by dividing the concentration of catalyst by the mean diameter of the suspensoid particles.

We have already noted from the preceding considerations that it is not strictly accurate to develop a relationship between reaction velocity and concentration of added catalytic material in heterogeneous catalysis, and that better agreement is to be expected when the superficial area of catalyst is substituted for the mass concentration.

The second factor of importance to be noted is the distribution of this catalytic material throughout the medium in which the reaction is taking place. In those cases in which solid surfaces are utilised as catalysts the reaction velocity is governed by two factors : (a) the rate of diffusion of reactants to the surface, or of the products of reaction away from the surface, and (b)

the rate of chemical action actually taking place at the catalytic surface. Frequently, the diffusion rate is extremely slow, whilst the catalytic activity is high. Under such conditions, comparison between different catalysts is impossible, since the rate of diffusion alone governs the velocity of the reaction.

When colloidal suspensions or emulsions are used as catalytic agents the active surface is not entirely immobile, as is the case in heterogeneous catalysis at solid surfaces, and so, in virtue of the Brownian movements of the sol particles, an enhanced apparent activity results.

The magnitude of the Brownian movement at any fixed temperature is dependent on two factors, the diameter of the sol submicron and the viscosity of the medium, as can be observed from the following figures obtained by Zsigmondy for gold sols.

Diameter (in $\mu\mu$).	Amplitude (in μ).
6	> 10
10	3—4
35	1—7

From Svedberg's researches on the influence of the medium on the amplitude of motion, a general relationship between viscosity and the amplitude may be obtained :

Medium.	Amplitude (in μ).	Absolute viscosity. $\eta \times 10^2$
Glycerol	0	83
Isobutyl alcohol	0·6	3·93
n-Propyl alcohol	0·7	2·26
Water	1·1	1·02
Ethyl acetate	2·0	0·46
Acetone	3·1	0·32

The second type of heterogeneous catalytic reactions which present still fresh and varied problems includes those in which the reactants are forced through a bed of granular contact material, the effluent gases or liquids being then submitted to analysis. Many examples of such reactions are to be found in technical practice, such as the catalytic process for the preparation of ammonia, hydrogen from water gas, the removal of calcium and magnesium salts from hard waters by sodium zeolites or chlorine from hydrochloric acid. The advance to be recorded in the scientific investigation of the hydrodynamics of the problem is not considerable.

It is at once evident that if a volume, V, of reactants be passed through a volume, v, of material per hour the "space velocity" or the volume of gas passed through unit volume of catalyst is $\frac{V}{v}$ litres (or c.c.) per litre (or c.c.) per hour. The "space velocity," or S.V., is an important characteristic, especially for technical purposes, and a clear statement of the space velocity is necessary when the feasibility of any process in under discussion. A closer analysis of this definition will, however, indicate that a certain amount of uncertainty is attached to this conception. It must be understood that the S.V. (space velocity) is always referred to the reactants at normal temperature and pressure, a matter of considerable importance when the reaction takes place in the vapour or gaseous state at elevated temperatures. Again, the conception of "reactant" permits of a certain degree of latitude. Thus, in the synthesis of ammonia from nitrogen and hydrogen in the stoichiometric ratios 1 : 3 both the gaseous constituents take part in the reaction, and since the stoichiometric relations are not altered after catalysis, both gases are to be considered as reactants. In other cases, such as in processes of hydrogenation, of selective combustion, or of the conversion of water gas into hydrogen and carbon dioxide in the presence of steam, the question arises as to whether the S.V. should be referred entirely to the reactant, *i.e.* the substance undergoing hydrogenation or combustion, or again to the carbon monoxide in the water gas. Thus, in the case of the water-gas conversion, the quantity of hydrogen in the gas or of steam employed might conceivably modify profoundly the velocity of reaction at the surface of the catalyst.

The procedure generally adopted is to refer the S.V. to some important constituent of the reactants. Thus, in the water gas reaction, the S.V. may be taken from the mean of the total volume of gas entering and leaving the catalyst mass corrected to N.T.P. after condensation of the steam, whilst in cases of hydrogenation, of, say, an oil, the S.V. would be referred to the mass of oil hydrogenated per unit volume of catalyst space or per unit mass of catalyst.

From the space velocity a second figure, no less important for technical operations, may be obtained, namely, the "space time yield," or S.T.Y. If the fractional conversion of reactants accomplished by a single passage through the catalyst mass at a space velocity of V be R, then the space time yield or the yield in litres of desired product per litre of catalyst space per hour, will be $R\ V$. In many cases, for convenience, the S.T.Y. is expressed in kilograms per litre of catalyst space per hour, or other similar units which give a numerical value to the product $R\ V$.

It may be observed that there is a relationship between R and V, since, for low values of V, the equilibrium under the conditions of operation is arrived at and R attains its maximum value. With an increase in the space velocity, equilibrium amongst the reactants may not have time to establish itself during the passage through the contact mass, and, with exceedingly high space velocities the composition of the reactants will scarcely be affected by such passage. Thus, to attain a maximum value of the product RV, it is not necessarily or indeed always desirable to limit the space velocity to such low figures as may be necessary to ensure attainment of equilibrium. Higher values for the S.V. and a lower conversion may give a greater output per hour. The RV, V curve will consequently assume some such form as the diagram above (Fig. 4).

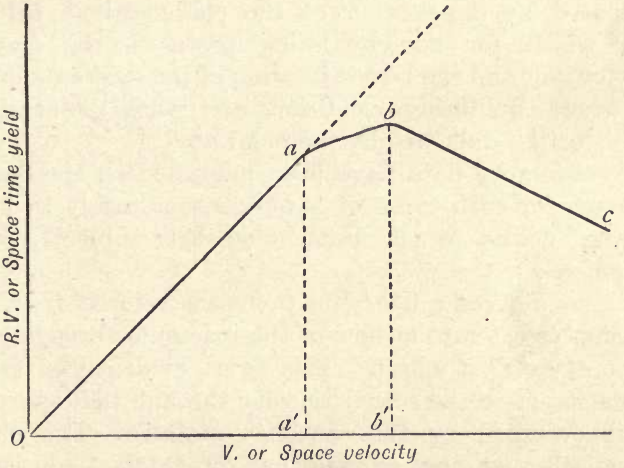


FIG. 4.

(i) The region O to a, in which equilibrium is established at all velocities up to a space velocity of a', whence the product $R\,V$ is proportional to V. (ii) The region a to b, where from space velocities a' to b', equilibrium is not established and the percentage conversion gradually falls off, the product $R\,V$, increasing, however, with increasing values of V. (iii) The region b to c, where, with exceedingly high space velocities, the rate of diminution of R, the fractional conversion, exceeds the rate of increase in the space velocity with a consequent decrease in hourly output.

In all circulating processes the optimum space velocity is represented by the point b' on the characteristic $R\,V - V$ curve, whilst for non-circulating processes the maximum hourly output and the best utilisation of the reactants (in those cases where equilibrium conditions are desired) is attained at space velocities indicated by the point a'.

No satisfactory data have been published on the design of converters for such types of heterogeneous catalysis, but the following points which bear upon this subject may be mentioned.

We have derived a figure for the space velocity from a consideration of the rate of flow of the reactants through a given volume of catalyst space. This figure evidently gives us no information as to the actual velocity through that space, since part is occupied by the catalytic material. For purposes of calculation we may assume that the catalyst consists of a number of uniform spheres, and, further, that they are packed in a simple and regular manner in the catalyst chamber.

It can be easily shown, for the simplest type of spherical packing, viz., point contact in sets of three, thus :

that the free space unoccupied by the spheres (assumed inelastic and incompressible) is 33·5 per cent. of the total volume occupied and is independent of the diameter of the spheres, whilst the free cross sectional area is 9·55 per cent. of the area of the catalyst chamber and is likewise independent of the diameter of the spheres. The dependence of the area of contact exposed by the surface of the spheres on the diameter of the individual is exemplified in the following curve (Fig. 5). The advantages of fine packing are clearly demonstrated.

The works of O. Reynolds on gravitational theory, and of Pope and Barlow on chemical crystallography, may be consulted for other types of spherical packing. They will be of use in giving an orientation into the problems of arrangement of the catalyst bed, but their utility is limited by the deviations of the catalytic material from spherical shape.

It is evident that for a S.V. of V, the true space velocity is approximately $3\ V$, when due allowance is made for the space occupied by the catalytic material, and that the linear velocity in metres per second may be obtained by calculating the rate of flow in a tube one-tenth the cross sectional area of the converter. In technical design, a linear flow rate of 10 metres per second is frequently taken as a convenient basis for calculation of gaseous reactions. Although fine division of the catalyst is desirable from the point of view of increasing the superficial area per unit volume of converter space, and although it may be possible to preserve uniform and approxi-

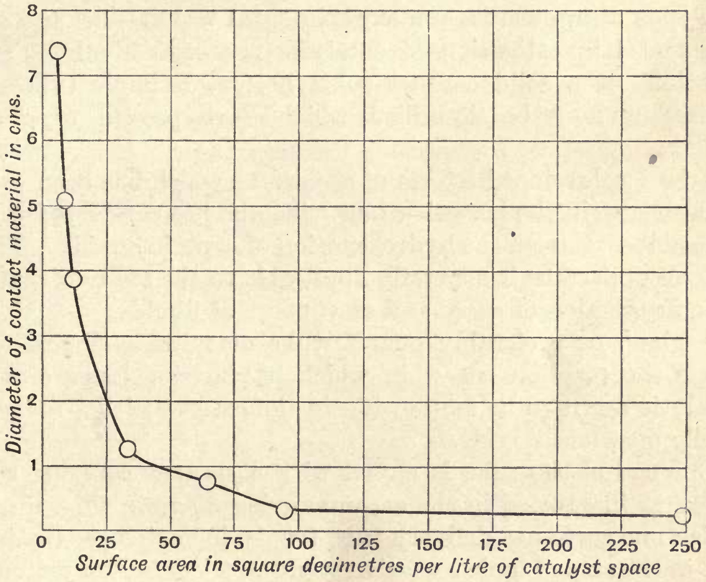


FIG. 5.

mately spherical packing in fine grained material, yet the increased skin friction caused by the great extension of surface to which the reactants are exposed during their passage raises the value of the frictional loss or back pressure in the converter to such a high figure as to preclude economic working. A second objection of a practical nature to undue reduction in catalyst size may be raised in that even coarse powders are very prone to removal by passage of the gaseous reactants, and are liable to exhibit the phenomenon of "channel formation" due to slight unevenness in the distribution of the material.

Types of apparatus for experimental work.—For the experimental investigation of catalytic processes involving gas reactions at a solid contact substance, two simple types of apparatus may be described which have proved of great utility.

Sabatier developed a form of apparatus which has been used with success in the investigations which he has conducted with his collaborators on the hydrogenation of organic liquids. This type of apparatus is generally applicable to the study of catalytic interaction of gases and of vapours of liquids.

A glass, or preferably quartz, tube of suitable dimensions forms the reaction space, in which is placed a layer of the catalytic agent to be employed—in the case of nickel a layer of the unreduced oxide.

One end of the tube is closed with a stopper carrying two tubes, as illustrated in the accompanying diagram (Fig. 6), of which one serves as delivery tube for the incoming gas (hydrogen in the case of hydrogenation studies), the other for delivery of the liquid, or of the gas to be investigated. In the case of liquids, a capillary tube is employed, the liquid being stored in the vertical tube, *T*. The rate of flow of liquid may be regulated by varying the diameter of the capillary and the height of liquid in the reservoir. Sabatier recommends that the inflow of liquid into the reaction space be constant by arranging that it does not leave the capillary in drops. By allowing the end of the capillary, *C*, to touch the inside of the reaction tube this may be readily attained. If the reservoir, *T*, be connected with a vessel of considerable dimensions the height of liquid, *A B*, may be maintained reasonably constant over long periods.

The reaction tube is heated in any suitable manner, either by gas flame, as in an organic elementary analysis, or more conveniently for the attainment of an even temperature by means of an electric resistance furnace. In the latter case, where the heating is uniform around the tube, the catalyst may be inserted as a plug in the reaction space as alternative to the layer of material employed in the gas-heated tube. The heating should extend sufficiently far along the tube to allow of vaporisation of the incoming liquid at *C*.

With sufficiently volatile liquids, an alternative arrangement is possible in which the mixture of the gas and vapour is obtained by allowing the former to bubble through the liquid, passing thence direct into the reaction space. By regulation of the temperature of the liquid and by ensuring saturation of the gas at the given temperature, from a knowledge of the vapour pressures of the liquid, a definite ratio of gas to vapour may be readily attained. The authors have found this a suitable method of introducing definite quantities of steam and alcohol vapours into the reaction mixture. It has been found, however, advisable in the case of steam, first to supersaturate the gas with steam by passage through water maintained at a temperature higher than that required to give the definite ratio, and then to pass the supersaturated gas through a further quantity of water maintained at the requisite temperature.

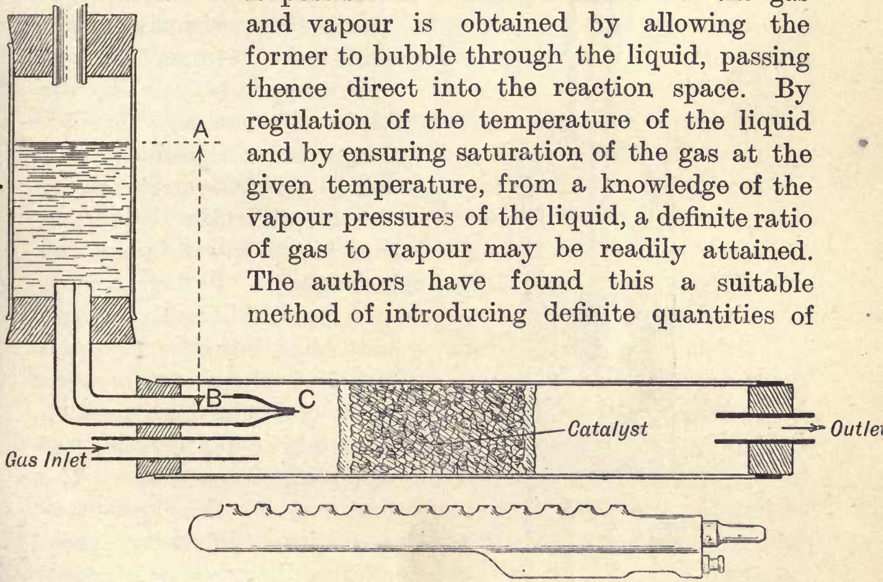


FIG. 6.

Sabatier, in the case of solids which are readily vaporised, places the material in porcelain boats inside the reaction space some distance before the catalyst mass. The incoming gas carries along with it the vapours of the solid arising from the heated boats.

The temperature employed may be determined according to Sabatier by means of a thermometer placed alongside the reaction tube, when the latter is embedded for evenness of temperature distribution in a layer of heated magnesia or fine sand. Alternatively, it may be placed inside the reaction vessel, in which case, however, there is difficulty in altering its position to determine the temperature at various points. With the latter alternative, a thermocouple is more useful than a mercury thermometer, owing to the difficulty of reading the latter when inside the tube.

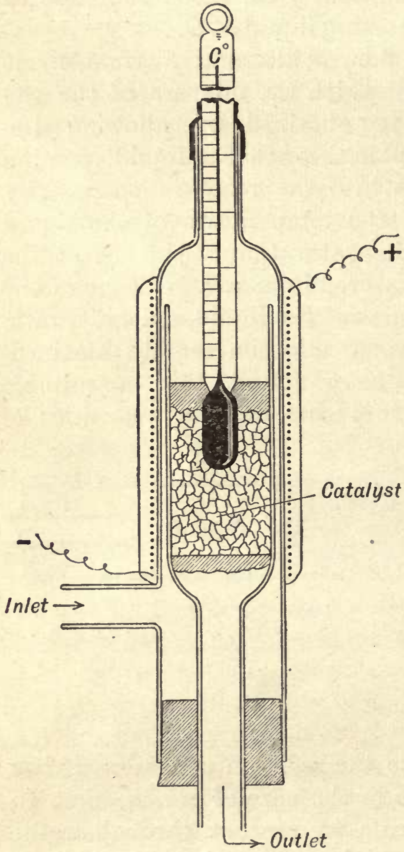


Fig. 7.

A modified form of apparatus has been largely used by the authors, more especially for the investigation of catalytic gas reactions at different temperatures. The features of the apparatus are its simplicity and adaptability, ease of temperature control and observation, as well as evenness of temperature distribution. The accompanying diagram (Fig. 7) illustrates the salient details of the apparatus. The outside glass or silica tube is electrically heated by means of a resistance wire suitably insulated and lagged. The upper end of the tube terminates in a length of tubing of narrower bore sufficient to pass the thermometer or thermo-couple, which may be adjusted in position at any suitable height. The catalytic material is contained in an inner concentric tube which, when in position, allows of a narrow space between the inside of the heater tube and the outside of the catalyst tube through which the gases pass up from below and are thus brought to the desired temperature. By this arrangement, apart from the radiation across the gas space, the heating of the catalyst material is caused by the incoming gases, and so can be the more easily regulated. Also, the charging of the reaction space with the contact body is more readily effected than in the apparatus designed by Sabatier. Large sizes of this type of catalyst furnace, constructed in iron with suitable modifications, have been employed with considerable success in experiments upon a semi-technical scale.

The contact mass: catalyst supports.—The form of the catalytic material is a factor of essential import in the problem of successful catalysis. Stress was laid in the preceding chapter upon the relation between physical condition and activity. Examination will show that efficient catalytic agents are, in general, porous, amorphous materials. The porosity of the material results in a greater surface per unit of bulk and the amorphous condition of the catalyst is, in all probability, a cause of its increased activity. For, as the recent researches on the *X*-ray spectra of crystals have shown, crystalline form is associated with a definite arrangement of atoms in the crystal, arising, doubtlessly, from the mutual saturation of the force fields of the various component atoms. With an amorphous substance, this mutual saturation of the residual valencies is absent, with the probable result that the material is in a more active condition catalytically.

For small scale experiments, the utilisation of catalytic material in the form of a porous, coarse powder is generally quite easily attained. If the powder be too fine, considerable resistance is offered to the passage of the gas, and this frequently results in channelling through the contact mass with a corresponding decrease in efficiency and lack of knowledge as to the quantitative details concerning the various factors of importance such as space velocity and linear velocity of flow. To avoid such eventualities, recourse is had to the incorporation of the catalytic mass upon a suitable support. Thus, finely divided platinum is frequently employed in the form of platinised asbestos, obtained by impregnation of asbestos fibre with a solution of a platinum salt followed by calcination of the mass to yield the metal in a fine state of division, and, yet, at the same time, in a form suitable for use. The use of inert supports also facilitates economy of catalytic material, an especial advantage in the case of expensive reagents.

A variety of substances have been employed in such a manner as support materials. In addition to the asbestos fibre already alluded to, mention may be made of glass wool and silica fibres, pumice, various porous, siliceous materials such as fire-clay, alundum and unglazed porcelain, the various forms of charcoal, anhydrous salts and porous oxides obtained by calcination of suitable minerals.

The choice of material to be employed is generally determined by processes of experimentation. As with the choice of catalysts generally, no sure guiding principles can be laid down. Experience shows, however, that in a great many cases use of a given catalyst support brings about a serious diminution in catalytic efficiency, generally attributed to a functioning of the support as a negative catalyst. Obviously, with a catalyst which is poisoned, for example, with sulphur, the presence of sulphur in the catalyst support is not permissible. The extraordinary sensitivity of certain catalysts to minute impurities restricts severely the number of possible supports. In reactions which are conducted at high temperatures, also, the possibility of interaction between catalyst and support material must be constantly envisaged. Especially in the case of oxide catalysts is this necessary, owing to the ease of combination with siliceous materials with formation of non-active silicates. In such cases catalyst supports which are basic in character are to be favoured. The ideal support, therefore, should be a porous material, free from impurities negatively catalytic to the contact body, incapable of interaction with the catalyst and, if possible, itself positively catalytic, even though feebly so, to the reaction in which it is to be employed. With such a material, suitably graded in size, the problem of form in catalytic material may readily be solved for all sizes of catalyst units.

CHAPTER IV

PROCESSES OF OXIDATION

The most varied and extensive application of catalysis to the problems of industrial chemistry has been made in the technical development of processes of catalytic oxidation.

Catalysts have been successfully employed to accelerate various processes of oxidation extremely dissimilar in character. Thus in processes of surface combustion, the catalytic material induces the *complete* combustion of gaseous and vaporised fuels for the production of intense and localised heat, whilst, on the other hand, the incandescent mantle exhibits similar localised combustion for the production of light. In those cases also in which the process of oxidation is reversible within the usual temperature range of operation, as in the oxidation of sulphur dioxide to sulphuric anhydride or of hydrochloric acid to chlorine and water, technical development was only possible after the discovery of catalytic agents which would accelerate the processes of oxidation at relatively low temperatures so as to ensure the maximum yield of the desired product at reasonable space velocities.

Another extending field for the technical development of processes of catalytic oxidation is to be found in the cases of *fractional oxidation*, where, by the choice of suitable catalytic material and the proper conditions of temperature, pressure, and concentrations of reacting substances, the reaction is caused to proceed along one path only, with the avoidance of possible side reactions or products of combustion of a higher or lower state of oxidation than is desired. Mention may be made of the technical processes for the oxidation of ammonia to nitric oxide, of hydrogen sulphide to sulphur, and of methyl alcohol to formaldehyde, as examples of such fractional oxidation. In all these cases, under adverse conditions, the yield of the desired product may be reduced to nil.

Processes of catalytic oxidation may also be *selective* in character. Thus, iron sulphide may be oxidised in the presence of the inflammable constituents of coal gas by the regulated admission of air under suitable temperature control. Mixtures of methane, hydrogen, and carbon monoxide may be analysed by the admission of oxygen, the combustion being conducted in such a manner that, by a suitable choice of catalytic material and operating temperature, only one constituent undergoes oxidation.

The classical experiments of Schönbein on autoxidation, in which the reaction velocity of the process of oxidation is extremely slow, opened up a new and interesting chapter in the theory of combustion. The significance of such processes of cold combustion will at once be apparent from a consideration of the mechanism of the corrosion or rusting of metals and the many remarkable cases of induced chemical reactions which accompany processes of autoxidation.

In the following pages, examples are given of the varied and manifold applications of catalysis to these diverse processes of oxidation. It will be noted that, as in many other cases, practice, as exemplified by technical development, has outstripped the theoretical treatment of the subject.

THE MANUFACTURE OF SULPHURIC ACID

The sulphuric acid industry is practically unique in the fact that the two processes employed on an ever-extending scale for its manufacture, the so-called "chamber" and "contact" processes, are both catalytic in operation and in the most modern plants the relative costs of production are practically identical. The "chamber" process, however, is confined to the production of the monohydrate, the maximum strength of acid obtainable being 98 per cent. H_2SO_4, whereas the "contact" process is more suitable for the production of "oleum," *i.e.*, sulphuric acid containing varying amounts of SO_3 dissolved in it, pure "oleum" or fuming acid having the composition $2SO_3{\cdot}H_2O$ or $H_2S_2O_7$.

The "chamber" process.—In this process the oxidation of sulphur dioxide to sulphuric anhydride by means of atmospheric oxygen is catalytically hastened by oxides of nitrogen, and is one of the very few cases of homogeneous catalysis in a gaseous system.

In actual operation a 6 to 12 per cent. mixture of sulphur dioxide in air obtained by passing a regulated amount of air over burning sulphur or sulphides such as pyrites, or spent oxide from gas works is brought into contact whilst still hot (400°) with a solution of nitrosyl sulphuric acid, by passage through one or two volvic lava- or flint-packed columns termed Glover towers, down which a stream of nitrosyl sulphuric acid is distributed.

The resulting mixture of sulphur dioxide, oxides of nitrogen, and air then pass into a series of leaden chambers into which steam or dilute sulphuric acid is blown by means of suitably shaped nozzles. The earlier rectangular reaction chambers, which would only produce one-sixth of a pound of sulphuric acid per cubic foot in twenty-four hours, are now replaced either by tangential chambers in which nearly 1½ lb. of sulphuric acid can be produced per cubic foot in the same time or by plate or packed towers in which the oxidation of the sulphur dioxide to the trioxide no longer takes place in the gaseous phase, but in the dilute nitric acid which is added to each tower. Although a considerable economy in space is gained in such tower systems, yet the extra installation costs and the increased resistance to the gas passage bid fair to militate against this advantage.

The spent gases from the reaction chambers are freed of all residual oxides of nitrogen by passage up a coke or stoneware ball-packed column, the Gay-Lussac tower, down which sulphuric acid is distributed.

The weak sulphuric acid from the lead chambers (ca. 65 per cent.) containing both oxides of nitrogen and nitric acid mixed with the nitrous vitriol from the Gay-Lussac tower is partially concentrated (to 78 per cent.) in the Glover tower, where the oxides of nitrogen are removed by the fresh gases and finally brought up to 98 per cent. strength by evaporation in Gaillard towers or by means of cascade concentrators.

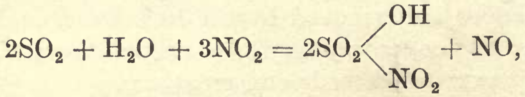
It is evident that under ideal conditions the oxides of nitrogen which are continually returned to the reaction chambers by means of the Glover tower should suffer no diminution during the cycle of operations. In actual practice, however, there is a small but continuous loss of the catalyst equivalent to from 1 to 4 parts of sodium nitrate in 100 parts of sulphur burnt. This deficit has to be continuously made good either by the addition of nitric acid to the Glover tower or by supplying oxides of nitrogen to the entering gases. In the latter case either small quantities of sodium nitrate (nitre) and sulphuric acid are placed in pots situated in the flue of the pyrites burners, or in the most modern practice, oxides of nitrogen, produced by the catalytic combustion of ammonia (see p. 90), are added at the base of the Glover tower.

The loss of oxides of nitrogen in the cycle is probably due to a variety of causes, amongst the more important of which may be mentioned :

(*a*) The presence of organic matter in the sulphur dioxide —a common occurrence when spent oxide is utilised.
(*b*) Loss in the sulphuric acid finally produced and at the exit of the Gay-Lussac tower.
(*c*) The reduction of nitric oxide to nitrous oxide or nitrogen by the coke packing in the Gay-Lussac tower and by decomposition in those parts of the contact chambers where the acid is under 40 per cent. strength.

An explanation of the mechanism by which the oxidation of sulphur dioxide to the trioxide is accomplished with the aid of oxides of nitrogen was first suggested by Davy in 1812, as a result of a series of experiments which had been conducted some six years previously by Clément and Désormes.[1] It was noted that when insufficient steam was admitted to the reaction chambers white crystals of nitrosulphonic acid were deposited ; Davy's hypothesis for the oxidation was based upon the intermediary formation of this acid according to the following equation :

(1)



$$2SO_2 + H_2O + 3NO_2 = 2SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right. + NO,$$

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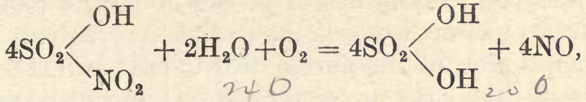
[1] See Lunge, Vol. I ; Raschig, *J. Soc. Chem. Ind.*, 1907, **10**, 965 ; 1911, **30**, 106 ; Partington, " The Alkali Industry," 1918.

the nitrosulphonic acid reacting with excess of steam and oxygen to form sulphuric acid :

(2) 

$$4SO_2\left\langle\begin{array}{l}OH\\NO_2\end{array}\right. + 2H_2O + O_2 = 4SO_2\left\langle\begin{array}{l}OH\\OH\end{array}\right. + 4NO,$$

240 200

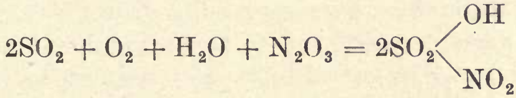
whilst the nitric oxide is re-oxidised to nitrogen dioxide as follows :

(3) $2NO + O_2 = 2NO_2$.

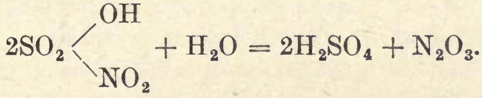
Lunge and Naef in 1884 found, on analysis of the chamber gases in the second and third chambers, that nitric oxide and nitrogen dioxide were present in equivalent proportions, behaving as N_2O_3.

(4) $NO_2 + NO \rightleftarrows N_2O_3$,

and suggested the following series of reactions to account for the formation and subsequent decomposition of chamber crystals.

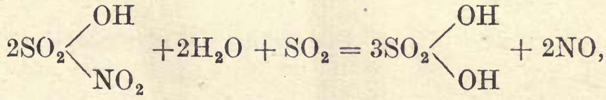
(5) 

$$2SO_2 + O_2 + H_2O + N_2O_3 = 2SO_2\left\langle\begin{array}{l}OH\\NO_2\end{array}\right.$$

(6) 

$$2SO_2\left\langle\begin{array}{l}OH\\NO_2\end{array}\right. + H_2O = 2H_2SO_4 + N_2O_3.$$

In the first chamber the gases are usually colourless owing to a deficiency of nitrogen dioxide. Lunge and Naef suggested that the removal of this constituent was taking place by means of a side reaction as follows :

(7) 

$$2SO_2\left\langle\begin{array}{l}OH\\NO_2\end{array}\right. + 2H_2O + SO_2 = 3SO_2\left\langle\begin{array}{l}OH\\OH\end{array}\right. + 2NO,$$

which would thus explain the presence of the nitric oxide in excess of the equivalent proportions demanded by equation (4). These comparatively simple reactions according to Raschig[1] and Trautz,[2] are not a sufficient explanation for all the pheno-

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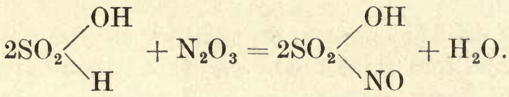
[1] *Annalen*, 1887, **241**, 200.

[2] *Zeitsch. physikal. Chem.*, 1888, **2**, 608.

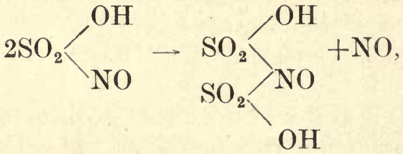
mena observed when sulphurous or sulphuric acids are agitated with oxides of nitrogen. It is common knowledge that in the usual nitrometer estimations a purple or pink coloration is nearly always present towards the end of the reaction.

The composition of the purple acid is unknown, but in all probability contains the nitroso-group, NO, to which its colour may be attributed.

Trautz postulates the formation of an unstable nitrosulphonic acid according to the following reactions :

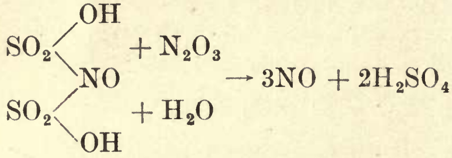


$$2SO_2{<}\begin{array}{l}OH\\H\end{array} + N_2O_3 = 2SO_2{<}\begin{array}{l}OH\\NO\end{array} + H_2O.$$

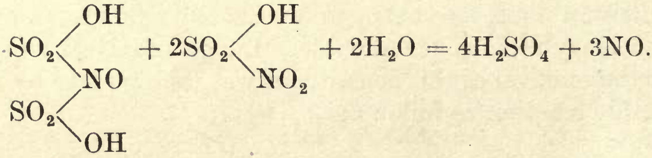


$$2SO_2{<}\begin{array}{l}OH\\NO\end{array} \rightarrow \begin{array}{l}SO_2{<}\begin{array}{l}OH\\NO\end{array}\\SO_2{<}\begin{array}{l}\\OH\end{array}\end{array} + NO,$$

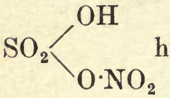
which is subsequently decomposed according to the following two side reactions :

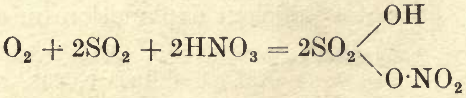


$$\begin{array}{l}SO_2{<}\begin{array}{l}OH\\NO\end{array}\\SO_2{<}\begin{array}{l}\\OH\end{array}\end{array}\begin{array}{l}+N_2O_3\\+H_2O\end{array} \rightarrow 3NO + 2H_2SO_4 \tag{1}$$



$$\begin{array}{l}SO_2{<}\begin{array}{l}OH\\NO\end{array}\\SO_2{<}\begin{array}{l}\\OH\end{array}\end{array} + 2SO_2{<}\begin{array}{l}OH\\NO_2\end{array} + 2H_2O = 4H_2SO_4 + 3NO. \tag{2}$$

The existence of a hypothetical nitrosulphuric acid  $SO_2{<}\begin{array}{l}OH\\O{\cdot}NO_2\end{array}$ has also been suggested by Lunge, formed by the interaction of nitric acid vapour on sulphur dioxide in the presence of air,



$$O_2 + 2SO_2 + 2HNO_3 = 2SO_2{<}\begin{array}{l}OH\\O{\cdot}NO_2\end{array}$$

It must, however, be admitted that our knowledge of the various side reactions which may occur between the oxides of nitrogen catalysts and the oxides of sulphur is far from complete, but it appears probable that the explanation advanced by Lunge and Naef represents the most important sequence of actions taking place under the conditions in actual chamber practice.

The "contact" process.—The early development of the lead chamber process for the manufacture of sulphuric acid took place in the years 1740 and 1750.

In 1812, Davy, who was the first to point out the true function of the oxide of nitrogen in the oxidation of sulphur dioxide, suggested the possibility of using platinum sponge as a catalyst for the same purpose. Phillips, in 1831, may claim to have been the pioneer in testing Davy's suggestion on the industrial scale, but owing to the rapidity with which his catalytic material became poisoned the process was abandoned until 1875, when Squire and Messel succeeded in making the process a technical success for the production of "oleum." These investigators utilised pure gases obtained by the decomposition of sulphuric acid on hot brick surfaces or by the combustion of sulphur, the sulphur dioxide being subsequently purified by washing with water under pressure.

The rapid development in the contact process during the opening years of the present century is chiefly due to the work of Kneitsch and Krauss,[1] who carried out a very systematic investigation on the reaction velocities and the conditions of equilibrium of the reaction:

$$2SO_2 + O_2 \rightleftarrows 2SO_3,$$

which was found by C. Winckler to be a reversible one. It was shown that the value of the equilibrium constant

$$K_p = \frac{P_{SO_3}}{P_{SO_2}\sqrt{P_{O_2}}}$$

where P_{SO_3}, P_{SO_2}, and P_{O_2} are the respective partial pres-

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[1] *Ber.*, 1901, **34**, 4069.

sures of the reacting constituents decreased with rising temperatures, as is observed from the following figures :—

Temperature.	K_p.	Temperature.	K_p.
430°	198·0	600°	14·9
450	187·7	610	10·5
500	72·3	627	5·5
528	31·3	700	4·8
553	24·1	727	1·8

By means of the general equation

$$\frac{d \log K_v}{dT} = -\frac{Q_v}{RT^2},$$

assuming that the value of Q_v, the heat of reaction, which according to Berthelot and Bodenstein[1] is equal to an evolution of 21,700 calories at the ordinary temperature, does not change seriously in value over the temperature range, we can calculate the value of K_v, and hence that of K_p for any desired temperature. The value of the integration constant can be obtained by taking an experimentally found value of K_p or by means of Nernst's heat theorem.

The fractional conversion, *i.e.* the values of the ratio $\frac{SO_3}{SO_2 + SO_3} = x$ could consequently be calculated when the magnitude of K_p had been determined. It is easy to show that the percentage conversion 100 x is equal to

$$100 \sqrt{P_{O_2}} \quad \frac{K_p}{1 + K_p \sqrt{P_{O_2}}}.$$

From this equation it is a comparatively simple matter to calculate the composition of the gas as it comes from the contact material in which equilibrium has been established, whilst the calculation of the final composition from an analysis of the entering gases can be made by means of the following equation :

$$100\,x = 100 . \frac{K_p}{K_p + \frac{1}{\sqrt{\frac{b - 0{\cdot}5\,ax}{100 - 0{\cdot}5\,ax}}}}.$$

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[1] Bodenstein and Finck, *Zeitsch. physikal. Chem.*, 1907, **60**, 1, 46.

where a and b are the percentages of sulphur dioxide, and oxygen in the initial mixture.

From these equations the following interesting facts can be deduced: first, that the ideal catalyst should be active at low temperatures, preferably below 500°, where the values of K_p are large; secondly, although an increase in the partial pressure of oxygen is beneficial in that it tends to raise the value of x nearer to unity, yet a limit is set to the quantity of air admitted by the effect of the diluent nitrogen. If we assume a mere trace of sulphur dioxide to be present in entering gases, *i.e.*, a is approximately zero and $b=20 \cdot 9$ per cent., then

$$\sqrt{\frac{b \quad - 0 \cdot 5\, ax}{100 - 0 \cdot 5\, ax}} = \sqrt{\frac{b}{100}} = 0 \cdot 457.$$

i.e.

$$100\, x = 100\, \frac{K_p}{K_p + 2 \cdot 2}.$$

For large values of K_p the yield is practically theoretical, but at 700° the value of $100\, x$ has sunk to 60 in spite of the very large quantities of oxygen present, whereas if no nitrogen had been present at all the value of $100\, x$ approximates to $\frac{100\, K_p}{K_p + 1}$, or 83 at 700°. The optimum results are obtained when the quantity of excess air admitted to the pyrites burners raises the oxygen content to the ratio $SO_2 : O_2 :: 2 : 3$, or three times the theoretical amount for complete conversion to the trioxide.

Having determined the conditions governing the oxidation of the sulphur dioxide, Kneitsch and Krauss investigated the reaction velocity in the presence of different catalytic materials. Utilising purified technical converter gas of the following composition, 7 per cent. SO_2, 10 per cent. O_2, and 83 per cent. N_2, the speed of conversion was determined when passed over various catalysts at different speeds and varying temperatures. In Fig. 8 (curves I and II) are shown the results of passing such a gas mixture over platinised asbestos in a porcelain tube at varying temperatures; it will be noticed that conversion with this, the most efficient of all the catalysts yet investigated, commences at 200° with a flow rate of 300 c.c. per minute (curve I) and at a little under 300° with a flow rate of 20,000 c.c. per minute (curve II), and as the flow rate increases a higher reaction velocity is required necessitating a higher temperature with a corresponding reduction in the equilibrium concentration of sulphuric anhydride obtainable. Curve III indicates the loci of the maxima of a set of the curves, utilising identical catalytic material, platinised asbestos and converter gas of similar composition but with different rates of passage.

It is evident that if some circulating system were employed, or alternatively a series of catalytic tubes were so arranged that the sulphur trioxide formed was removed after each catalytic treatment, the maximum conversion per unit of time would not be obtained with an operating temperature and speed of passage corresponding with the probable maximum conversion, but would entail a very high rate of passage with a relatively low conversion, the speed and temperature being so adjusted as to ensure the product, per cent. conversion × flow-rate being a maximum. Technical difficulties associated with the removal of the sulphur trioxide from a gas containing relatively large quantities of the lower oxide appear to have prevented the realisation of this possible procedure.

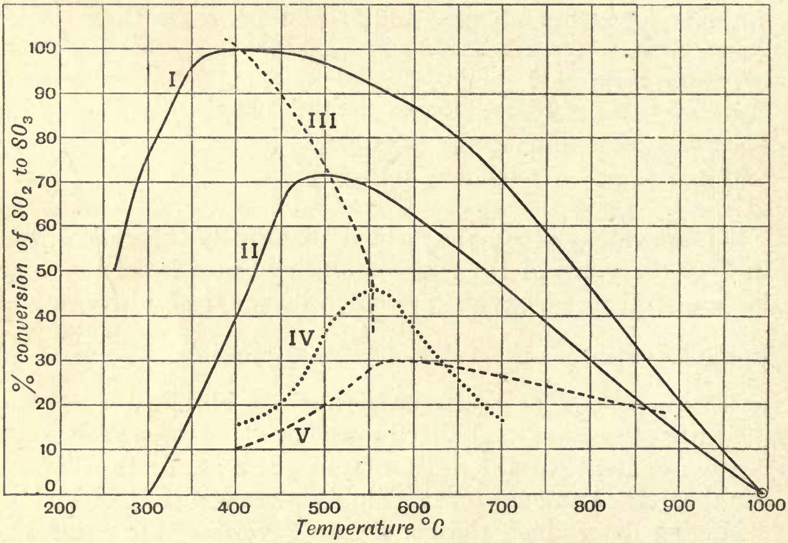

FIG. 8.

Curve IV indicates the results obtained with burnt pyrites

(CuO,Fe_2O_3) as contact material with a flow rate of 500 c.c. per minute, whilst curve V shows the low duty obtained with broken porcelain as catalytic agent.

We have already referred to the employment of purified converter gas by several investigators. Squire and Messell appear to be the first to have realised the significance of catalyst "poisons" in the ordinary gas, and used, as an alternative, sulphur dioxide prepared from some purer source. The Badische Anilin- & Soda-Fabrik successfully solved the technical problem of purifying ordinary converter gas from poisons, notably arsenic, antimony, phosphorus, and lead, by steam treatment, cooling, and washing. The resulting gas is so purified as to be optically pure, showing complete freedom from suspended matter even when subjected to intense illumination.

Since the optimum conversion temperature lies between 400° and 450°, it was evident that for the successful technical development of the process the entering gases should strike the catalyst at a temperature approximating as nearly as possible to this, and should leave the catalyst at sensibly the same temperature. The reaction, however, is strongly exothermic, 21,700 calories being evolved per gm. mol. of sulphur dioxide converted. The Badische converter was accordingly constructed of relatively narrow iron reaction tubes, 10 per cent. platinised asbestos being employed as catalytic material. The maximum radiation was thus obtainable by this method. A part of the inflowing gas, passing externally over the tubes in a counter current direction, was so adjusted as to regulate the catalyst temperature and at the same time assisted in heating up the remainder of the entering gases.

In the Mannheim process developed by Clemm and Hasenbach a preliminary conversion is effected by passage of the gases over burnt pyrites at from 500° to 600° where some 45 per cent. conversion is effected. The gases freed from the sulphuric anhydride by absorption in strong sulphuric acid are then passed on to the lower temperature platinum catalyst. A dual advantage is thus obtained. In spite of the lower duty obtained with the burnt pyrites catalytic material on account of the somewhat elevated reacting temperature, this catalyst is not so sensitive to traces of poisons as the platinum and is a comparatively cheap material to utilise. As a further consequence, a very pure gas passes on to the platinum converter, and since nearly half of the sulphur dioxide has already been removed, the temperature of this catalyst can be easily adjusted within the prescribed limits.

Of the various catalytic materials employed to accelerate the oxidation of sulphur dioxide to sulphuric anhydride, platinum is undoubtedly the most active, and much ingenuity has been displayed in obtaining the maximum yield possible with the aid of relatively small quantities of this somewhat expensive material.

In the Badische type of plant where platinised asbestos is utilised, the platinum is frequently deposited from the platinic chloride by means of a formate solution according to the method originally suggested by Loew.[1]

The Tenteleff process utilises a series of coarse asbestos string mats some 2 feet by 3 feet in area, impregnated with platinum black, from twelve to twenty-five being used as the contact mass; the quantity of platinum distributed on each mat varies from 60 to 65 grams.

The Schröder-Grillo contact material[2] is undoubtedly the most ingenious of any which are in operation, producing a very active form of platinum black and at the same time exposing a large area of catalytic surface.

The heptahydrate of magnesium sulphate is soaked in a solution of platinum salt and heated up in the presence of sulphur dioxide, the reduction of the platinum being thus effected. At the same time, the salt undergoes dehydration and puffs up in a remarkable manner, the surface becoming covered with a very thin layer of platinum. From 0·2 to 0·3 per cent. of platinum on the magnesium sulphate is sufficient to form an excellent contact material. With 5 grams of platinum one ton of "oleum" can be produced per day with a loss of only 20 milligrams of metal.

Of the various other catalytic materials suggested, it seems that only burnt pyrites has actually been used on an industrial scale. By reference to the patent literature, the problem of finding some other non-platinum catalyst more active than burnt pyrites is still the object of investigation. Amongst the more important materials suggested may be mentioned the oxides of

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[1] *Ber.*, 1890, 23, 289.

[2] *J. Soc. Chem. Ind.*, 1903, 22, 348.

copper, vanadium, uranium, chromium, nickel, and cobalt, frequently incorporated with aluminium, beryllium, zirconium or zinc oxides, or the rare earths, such as didymia or ceria. It is of interest to note that oxide of arsenic itself, although a poison for platinum, is a comparatively good catalyst at somewhat higher temperatures. More novel is the suggestion to incorporate with the catalytic material some body which readily absorbs sulphur trioxide at the temperature employed and disengages it again at a higher temperature.

Various theories have been put forward to explain the mechanism of the contact process; it is usually assumed that the intermediary formation of the platinum oxide, PtO, or the more transitory and possibly hypothetical dioxide, PtO_2, suggested by Wöhler and Engler, plays the important *rôle* in this catalytic operation according to the following cycle:—

(i) $2Pt + O_2 \rightarrow 2PtO + 2SO_2 \rightarrow 2Pt \cdot 2SO_3$.

(ii) $Pt + O_2 \rightarrow PtO_2 + 2SO_2 \rightarrow Pt \cdot 2SO_3$.

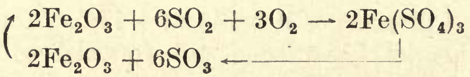
Wieland, however, has laid stress on the "hydration" theory of chemical action. Since perfectly dry sulphur dioxide and oxygen do not combine, he represents the oxidation of the sulphur dioxide as subsequent to a previous hydroxylation:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$H_2SO_3 \rightarrow SO_3 + H_2$$
$$2H_2 + O_2 \rightarrow 2H_2O.$$

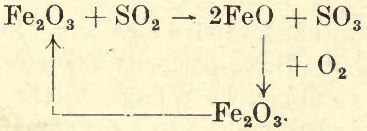
It may be urged in favour of this view that in those cases where intermediate products of oxidation can be isolated and analysed—especially in organic reactions where the hydroxyl groups can be fixed and characterised as soon as they are formed by the substitution of a suitable non-reactive grouping—the evidence for hydroxylation as a stage in oxidation is remarkably strong.

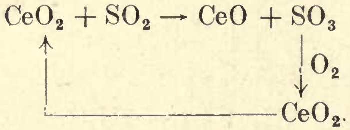
It is extremely probable that adsorption phenomena exert a by no means inconsiderable influence on the rate of the reaction. The interesting observation has been made that the activity of catalytic platinum prepared on the Schröder-Grillo system is very considerably elevated if subjected to agitation by some means such as a short oscillation of the containing trays. It is suggested that a more effective removal of the condensed film is thus obtained by subjecting the surfaces to gas flows continually altering in direction relative to their faces, thus ensuring a higher apparent catalytic activity.

With oxide catalysts such as oxide of iron, it is generally assumed that the formation of an intermediary sulphate occurs according to the following cycle:



It is evident, however, by reference to the list of oxides suggested as suitable for technical processes that practically only those elements are included which possess at least two oxides and, as in many other catalytic processes, we are equally justified in assuming the catalytic activity to be due to an oscillation between the two states of oxidation.





It must also be admitted that the explanation formed on the "intermediary sulphate" theory is not very satisfactory in the light of the researches of Bodenstein and Suzuki,[1] who showed that the first products of the distillation of ferric sulphate are SO_2 and O_2, which then react in the presence of ferric oxide to produce SO_3, whereas SO_3 should be the primary product on this hypothesis.

Use of catalysts in the Hargreaves process.—Hargreaves and Robinson in 1870 introduced a method for the manufacture of salt cake (Na_2SO_4) by the interaction of pyrites burner gas and air on hot salt at 525°.

Above 600° fusion of the salt occurs, thus setting a limit to the

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[1] *Zeitsch. Elektrochem.*, 1910, **16**, 912.

temperature for the reaction. To accelerate the reaction at low temperatures, various catalysts have been proposed, notably ferric oxide[1] and copper oxide.[2]

It was suggested that the salt should be moistened with a solution of the sulphate of the metal so as to obtain an activated salt containing from 0·1 to 1·0 per cent. of the metal.

The experimental investigation of the influence of copper and iron salts was reported by Conroy.[3] The conclusions reached are thus summarised. Salt is decomposed by a mixture of sulphur dioxide and air at a temperature below 600° to yield sulphate and chlorine. Decomposition in glass vessels is exceedingly slow. With addition of 0·25 per cent. of copper in the form of sulphate, reaction begins at 400° and increases in amount with temperature.

The rate of action at 600° was roughly 50 per cent. greater than at 450°. Increased concentration of copper increased the rate of reaction. It was shown that 0·5 per cent. of iron as sulphate was catalytically equivalent to 0·25 per cent. of copper. Magnesium and aluminium sulphates were without action. With suitable gas speed, reaction was quantitative, all sulphur dioxide being retained. At higher speeds of passage, both chlorine and sulphur dioxide escaped. The conversion to sulphate could be carried to completion.

In Conroy's view, the salts of copper and iron probably act by inducing the combination of sulphur and oxygen to form sulphuric anhydride, since, by inserting platinised asbestos in the inlet end of the reaction tube the ratio of the chemical equivalents of chlorine to sulphur dioxide and sulphur trioxide rose from 1 : 14 to 1 : 1. This method of working the process, viz., by passing a mixture of sulphur dioxide and air through vessels containing alternately a contact substance to produce sulphuric anhydride and salt was patented by Deacon in 1871.[4]

To check fusion, Clemm proposed[5] to admix clay with the salt, utilising copper oxide or ferric oxide to aid the reaction.

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[1] Hargreaves, 1886.

[2] Kruhing and Dernoncourt, 1897; Clemm, 1899; and Hargreaves, 1907.

[3] *J. Soc. Chem. Ind.*, 1902, **21**, 304.

[4] B.P. 1908/1871.

[5] B.P. 15152/1899.

THE OXIDATION OF AMMONIA TO NITRIC ACID

During the period of the war, amongst all the belligerent Powers, this important catalytic operation necessarily attracted a great deal of attention owing to the world shortage of nitrates for explosive purposes. After the war the exhaustion of the Chilean nitrate deposits, the increasing demand for nitric acid for our growing industries in the various branches of organic chemistry and as nitrates for fertilisers, as well as the rapid strides recently made in the economic production of ammonia both as a coal by-product and in the form of cyanamide and pure ammonia manufactured by the Haber synthetic process, will all tend to make the technical operation of an ammonia oxidation plant not merely a war industry but an integral part of the economic development of the state.

The pioneer work on this problem was accomplished by the French industrial chemist, Kuhlmann, in 1839, but until Ostwald and Brauer published their researches in 1903, no progress was made in the technical development of the process.

During the last few years several systems have been developed on an industrial scale, yielding on an average an efficiency of conversion of from 90 to 95 per cent. Amongst the more important may be mentioned those of Ostwald and Brauer, Frank and Caro, and that of Kaiser. Modifications and improvements of these German processes have been developed by the Allied Government Research Departments and by private firms during the period of the war, effecting a combination of the best features of the respective plants.

The oxidation of ammonia is effected by the passage of an air–ammonia or oxygen–ammonia mixture over a catalytic material maintained at a suitable temperature.

The primary reaction may be represented by the following equation :—

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

Under the conditions of catalytic combustion the oxidation of ammonia is practically complete, as can be calculated from the Nernst heat theorem, assuming that the above equation is strictly reversible.

The heat liberated in the combustion of 4 molecules of ammonia under the above conditions is 215,600 calories at 17°. For a homogeneous gas reaction we can calculate from Nernst's equation the equilibrium constant :—

$$K_p = \frac{p_{NH_3}^4 \times p_{O_2}^5}{p_{NO}^4 \times p_{H_2O}^6}.$$

$$\text{Log}_e\ K_p = \frac{Q_0}{RT} + \frac{\Sigma\nu C_{0p}}{R}.\ \log_e T + \frac{\Sigma\nu\beta}{R} + \Sigma\nu\, i,$$

where Q_0 and C_{0p} are the heat of reaction and the specific heats of the reactants at absolute zero, $\Sigma\nu$ the algebraic sum of the number of molecules, and i the integration constant of the vapour pressure formula.

For C_{0p} we can approximate the value 3·5 given by Nernst. The chemical constants for O_2, NH_3, NO, H_2O are : 2·8, 3·3, 3·5, and 3·6 respectively and $\Sigma\nu i = -8{\cdot}4$. Correcting the heat of combustion, viz., 215,000 for a temperature of absolute zero, taking into account the change in the specific heat of the gaseous constituents with the temperature, Q_0 will be found to be equal to 216,300 cal.

For temperatures of oxidation between 500° and 1000°, the range usually adopted in technical plants, or a mean of 800°, $C_p = C_{0p} + 2\beta T$.

$$2\beta = \frac{C_{p800^\circ} - 3{\cdot}5}{800}.$$

$$\text{Hence } \log_{10} K_p = \frac{216{,}300}{4{\cdot}57T} - 1{\cdot}75 \log T + \frac{0{\cdot}007}{4{\cdot}57} T - 8{\cdot}4.$$

For log K_p we find :

T	log K_p
500°	−108
800	− 71
1000	− 61

It will be observed that even at 1000° the quantity of ammonia in equilibrium with the nitric oxide under these conditions is almost vanishingly small and quantitative yields should always result.

In practice, quantitative yields are never obtained for the following reasons :

(1) The time of contact of the air or oxygen–ammonia

mixture with the active surface of the catalyst may be too long. Under these conditions the nitric oxide formed by combustion with the ammonia will commence to dissociate and establish equilibrium according to the equation,

$$2NO \rightleftarrows N_2 + O_2.$$

This equilibrium is likewise governed by the temperature of the gas and is the basis of the arc process of fixing atmospheric nitrogen.

According to Nernst and Haber, the equilibrium amount of nitric oxide formed in air at 2000° is only 1·0 per cent. varying to 10 per cent. at 4140°, but is practically negligible at the working temperatures of the ammonia oxidation process (circa 0·001 per cent. NO at 800°). On the other hand, the velocity with which equilibrium is established is greatly increased by a rise in temperature, and the gas containing the high concentration of the nitric oxide produced by combustion of ammonia must be rapidly cooled to decrease the velocity of the normal decomposition. It is evident from this consideration that the catalyst should be maintained at a low temperature and that the period of contact of the gases with the catalyst be as short as possible.

(2) Part of the ammonia may escape contact with the catalyst. Undecomposed ammonia present in the effluent gases will react with the nitrous acid formed on the condensation of the nitrogen oxides in water, with the liberation of nitrogen :

$$NH_3 + HNO_2 = N_2 + 2H_2O.$$

Twice the amount of nitrogen originally present in the escaping ammonia will thus be lost.

(3) Absorption of the oxides of nitrogen may not be complete.

Ostwald and Brauer's process.—This system has been largely developed in Germany, whilst independent factories were established by the Nitrogen Products Co. at Vilvorde in Belgium, Angoulême in France, Dagenham in England and at Legnano in Italy. As catalytic material, platinum foil is used in the form of a corrugated roll, about 2 cm. deep ; 50 grams in weight, loosely inserted in the end of a nickel tube some 2 metres long, and 9 cm. in diameter (solid drawn nickel is said to be preferable to welded tube). The nickel tube through which the ammonia and air mixture (circa 5 per cent. NH_3) passes is enclosed by an enamelled iron tube somewhat wider in diameter, the whole system thus acting as a simple form of heat interchanger. The ammonia–air mixture is thus heated up to a temperature of 650° before striking the platinum roll, which is maintained at 650—700° by the heat of combustion of the ammonia. The eflowing gases, consisting of nitric oxide, nitrogen and residual oxygen from the air, which is added in excess, are cooled down, and, after sufficient time of storage to ensure that the oxidation of the nitric oxide to nitrogen dioxide is complete, are passed into the nitric acid absorption towers.

Frank and Caro's process.—The disadvantages of the original process, namely, the lack of control of the catalyst temperature and the relatively large amount of platinum required to produce a given quantity of nitric acid (50 grams will only produce some 30 tons per annum), led Frank and Caro to construct a form of converter in which a more economical form of utilisation of the catalyst (in this case platinum also was used) was attempted.

The converter of rolled aluminium consisted of a rectangular column containing baffle plates equally spaced and terminated by a conical hood of the same material. A fine platinum gauze (80 linear meshes to the inch of wire 0·0026 in. diameter) was stretched across the converter column and by means of silver leads could be maintained at a uniform temperature (circa 650°) by the passage of an electric current. With the catalytic material in this form a somewhat richer air–ammonia mixture (9–11 per cent.) could be dealt with and the converters constructed in considerably larger sizes. Technical units have been constructed up to 1 square foot in cross section, whilst in America experiments on still larger units have been carried out. The output per square foot of catalyst surface is approximately 700 kilograms of nitric acid per 24 hours, whilst the weight of platinum is less than 40 grams per square foot. The yield is stated to average 92 per cent.

Kaiser's process.—From 1911 to 1916 Dr. Kaiser, as a result of investigations carried out on a technical scale at Spandau, near Berlin, put forward somewhat startling claims for a process developed by him.

In this process the single layer of platinum gauze is replaced by four separated layers of similar material, the total thickness not exceeding 0·5 to 0·6 mm. Electrical heating is dispensed with and the air previous to admixture with the ammonia is preheated by means of a coke fire to 300–350°. Kaiser's original claims of efficiencies, exceeding 100 per cent. owing to the simultaneous autoxidation of atmospheric nitrogen, have now been shown to be fallacious and it appears possible that these were advanced only to overcome certain difficulties attached to the patent protection of his process.

The process was installed in a somewhat modified form by Saposhnikoff at Kharkoff in Russia, where an overall efficiency of over 92 per cent. has been claimed. Recent experiments have also indicated that higher rates of gas flow and a consequent greater output per square foot of converter area are obtainable with multiple gauzes, although the actual output per gram of platinum is somewhat lower. The average yield per square foot of converter area with two gauzes per 24 hours is 1·5 to 1·8 metric tons of nitric acid (in all cases calculated as 100 per cent.).

Small plants using two or more gauzes are already installed in England for the supply of oxides of nitrogen in vitriol chambers and are giving 90 per cent. yields continuously.

It appears possible that the ultimate form of converter using a platinum gauze catalyst will embrace the following points :—

(*a*) At least two gauzes will be employed.
(*b*) The effluent gases will be used to preheat the whole or part of the incoming air prior to admixture with the ammonia vapour, or, alternatively,
(*c*) The air–ammonia mixture will be preheated by the exhaust gases in a non-catalytic metal heat interchanger, *e.g.*, aluminium or nickel.
(*d*) Starting will be accomplished electrically.

Certain of these features are embodied in one form of technical converter unit shown in the illustration (Fig. 9), and described by Partington[1] as follows : It consists of a top and bottom cone, with three rectangular body pieces between them, all in cast aluminium $\frac{1}{8}$ inch thick, the rectangu-

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[1] *J. Soc. Chem. Ind.*, 1918, 37, 337.

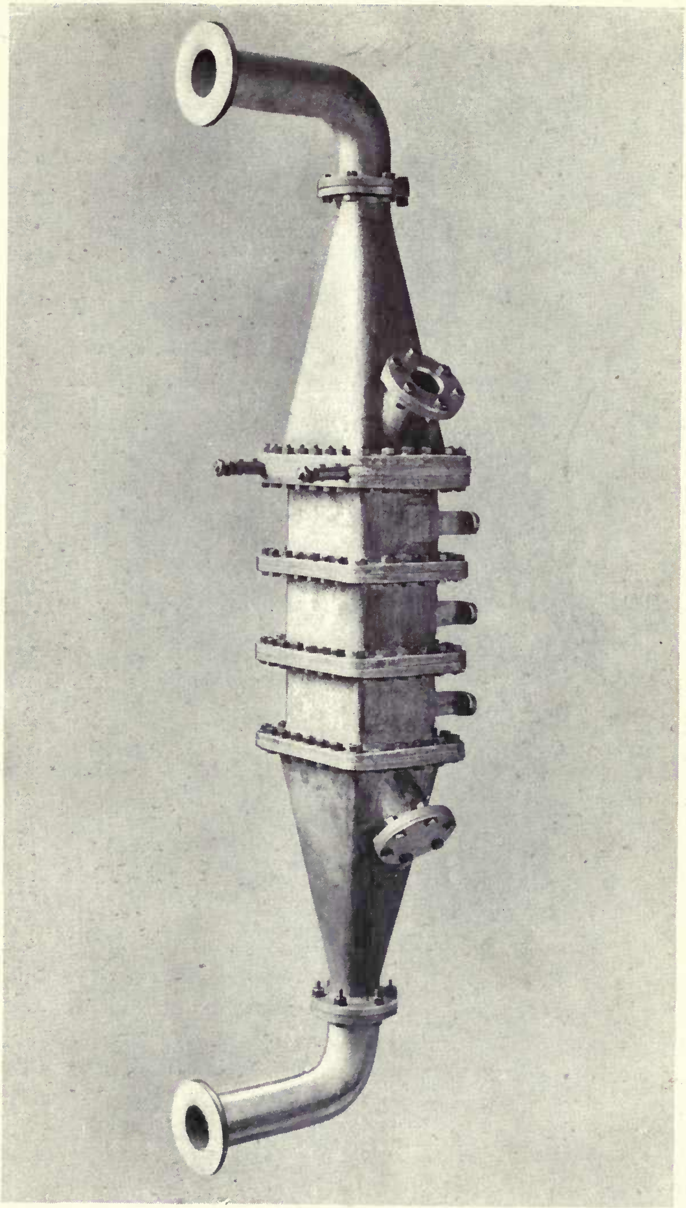

FIG. 9.

[*To face p.* 94

lar area exposed measuring 4 inches by 6 inches. The pieces are provided with flanges, ¾ inch wide, to facilitate bolting together, and three perforated baffles are inserted in all the junctions except that between the top cone and the top segment of the body, which is occupied by the catalyst frame. Though each cone possesses a sight orifice, 1½ inches in diameter, for reasons of standardisation, that in the top cone alone is used, and is provided with a mica window for inspection of the catalyst. Aluminium bends of 2 inches internal bore provide inlets and outlets for the mixture of air and ammonia at the bottom, and the oxides of nitrogen at the top, respectively. The overall length of the converter is about 4 feet and its weight is about 32 lb.

The air supply is obtained from a blower, and it is essential that the air and ammonia should be well mixed. If ammonia gas is used, it may be injected into the air stream through a nozzle, after both gases have been measured. In technical practice it is more convenient to use purified ammonia liquor containing 25 per cent. of ammonia, which is now a commercial article. The air is passed, together with a small amount of steam, into the base of a coke tower down which this liquor flows. The mixed gases are cooled in the upper portion of the tower, where the steam is condensed. The mixture of air and ammonia should be filtered, either by passage through a length of coke packing in the upper portion of the tower or through a filter packed with glass wool, which removes particles of dust. Oxide of iron particularly must be eliminated, as this has a deleterious effect on the platinum catalyst.

The most important part of the apparatus is the catalyst, which is fixed between the upper cone and body segment. It consists of one or more gauzes made of pure platinum wire, stretched across the converter at right angles to the gas flow. The wire used is 0·0025 inch in diameter, and is woven into gauze with 80 meshes to the inch. The gauzes are mounted in an aluminium frame. The reaction occurs during the very small interval of time in which the gases are in contact with the catalyst.

The operation of the catalyst must be initiated by heating the gauze, either by means of a non-luminous gas flame, or by heating electrically with suitable current conducted through leads attached to the opposite edges of the gauze. When the first method is used an orifice is provided in the upper body segment just below the gauze, which admits of the introduction of the flame, and is closed when the converter is in operation. The converter figured is provided with leads for electric current. When the reaction begins, the gauze is maintained at a red heat by the heat of oxidation, and the conversion proceeds uninterruptedly as long as the supply of air and ammonia is maintained. The platinum gauze may be used for about three months, after which it is desirable to replace it by a new gauze and to clean and refit. New gauzes are not very active at first, but acquire their full catalytic activity after a few hours' running.

THE CATALYSTS EMPLOYED IN THE OXIDATION OF AMMONIA

Platinum.—It will be noted that all existing technical ammonia oxidation plants employ platinum [1] as a catalyst, and many interesting observations have been made as to the catalytic activity of platinum for this purpose. Kuhlmann, in 1839, first noted that platinum sponge was more efficient than platinum black for the production of oxides of nitrogen, but that larger yields of nitrogen were obtained with the latter. Bright platinum is scarcely active. Ostwald and Brauer [2] continued Kuhlmann's researches and showed that the optimum results were obtained when bright platinum was coated with an almost invisible film of grey or black platinum and that only a short period of contact was necessary, *i.e.*, 0·01 second. Schick, in 1907, noted that platinised porcelain, of which the glaze was slightly fusible, permitting the coalescence of the platinum into minute droplets, was extremely active, and recent photomicrographic investigation of platinum gauze also indicates that there is a gradual increase in catalytic activity associated with the formation of minute craters on the metal, the lip of each crater being just tinged with "grey" or "black" platinum. By the use of such an active net the period of con-

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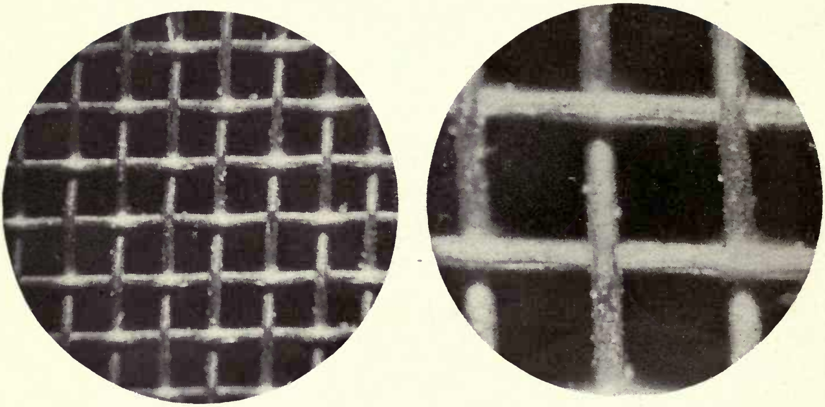
[1] Recent information from Germany indicates that the use of non-platinum catalysts has been largely developed during the last two years.—E. H. R.

[2] *Chem. Zeit.*, 1903, 27, 100.

Photomicrographs of Platinum Gauze.

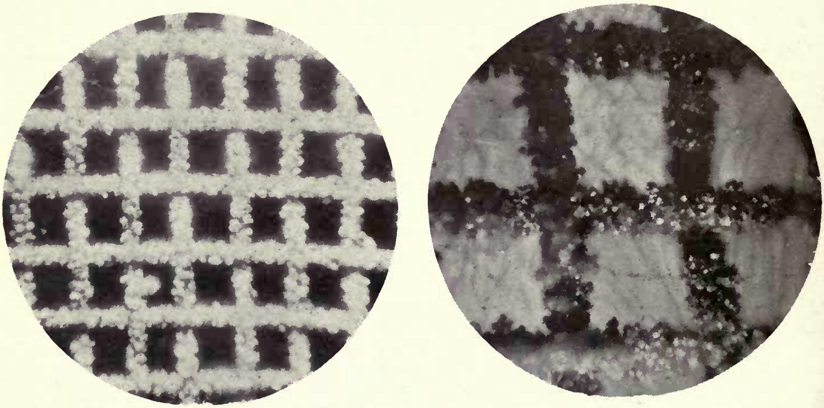


× 24.

Plain wire before use.

× 75.

Plain wire before use.



× 24.

After some weeks' use.

× 75.

After some weeks' use.

Fig. 10.

[*By permission of Messrs. Brunner Mond and Co., Ltd.*

tact may be reduced to as low a figure as 0·0006 second. The illustrations (Fig. 10) given show the changes in structure of a gauze during use.

It seems probable that the black or grey platinum is the active catalyst, but when present in large quantities it is liable to cause the formation of nitrogen either in the primary oxidation of the ammonia, or, as seems more probable, due to secondary decomposition of the nitric oxide.

Several instances of poisoning have been recorded, especially by sulphur compounds present in gas works ammonia, and by silica, phosphine, and acetylene present in cyanamide ammonia. The more recent experiments, however, appear to indicate that such volatile substances as sulphur, phosphorus, and acetylene are not negatively catalytic except in relatively large quantities, but that the more serious poisons or negative catalysts are the non-volatile impurities, *e.g.*, silica, ammonium phosphate, dust, oxide of iron, and the like. Probably for this reason platinum impregnated on pumice or asbestos has a remarkably low efficiency.

Non-platinum catalysts.—Kuhlmann, in 1839, noted the catalytic activity of oxides of copper, iron, and nickel for this purpose, whilst Du Motay[1] proposed the use of alkaline manganates, permanganates, bichromates, and plumbites.

Ostwald and Brauer, in the series of researches previously alluded to, indicated the activity of the oxides of manganese, lead, silver, copper, chromium, nickel, cobalt, vanadium, and molybdenum, but stated that they were all inferior to platinum in catalytic activity. Frank and Caro[2] proposed the use of ceria and thoria, whilst Wendriner suggested the black oxide of uranium, U_3O_8.

During the period of the war, research in the utilisation of non-platinum catalysts has been extremely active especially in America and Germany, where the dearth of platinum was somewhat acute. Although no non-platinum catalytic process has been assured of technical development,[3] nevertheless the results obtained on a small scale are sufficiently encouraging to justify their continuance.

Jones and Morton in the United States have reinvestigated Du Motay's alkaline plumbites, especially those of magnesium,

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[1] B.P. 491/1871.

[2] D.R.P. 234329.

[3] See *ante*.

zinc, cadmium, and aluminium, with success. Their reactivity towards metals and all forms of glass and silica at high temperatures is the chief objection to their use.

In England, Maxted[1] has investigated the use of oxides of iron admixed with certain promoters such as copper oxide, lime, or bismuth oxide. He has shown that the conversion of ammonia–oxygen mixtures can be accomplished in heated tubes, specially " activated " on the inside, with more than a 90 per cent. efficiency. The short life of the catalyst under these conditions is the chief drawback to his process. The use of oxygen instead of air is obviously only permissible in conjunction with a synthetic ammonia plant in which the oxygen fraction from the liquid air plant used in the preparation of the nitrogen would be available.

The Badische firm in Germany have investigated the effect of a great number of promoters on active or feebly active catalysts, such as tellurium and lead oxides on platinum, bismuth, chromium and cerium oxides on iron oxide.

It will be at once evident that " oxygen carriers " appear to be the *sine quâ non* for ammonia oxidation, and the enhanced activity of binary and ternary mixtures of the oxides of those elements which possess at least two or more well-defined oxides indicates some relationship in this case between the catalytic activity and the presence of an oscillating higher and lower oxide functioning as an oxygen carrier. The presence of a number of oxides evidently increases the temperature range of catalytic activity by affecting the stability of the oxides.

It is interesting to note that chromium oxide ex chromium salts is practically inert, but the oxide obtained by the ignition of ammonium bichromate exerts a very marked catalytic activity.

The observation of Ostwald and Brauer, namely, that the period of contact with non-platinum catalysts must considerably exceed that necessary for platinum, has been repeatedly confirmed. The practical difficulties associated with the uniform heating and at the same time ensuring a uniform stream line flow through a shallow bed of small briquettes or powders of such materials also presents grave technical disadvantages.

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[1] *J. Soc. Chem. Ind.*, 1917, **36**, 777.

THE OXIDATION OF HYDROCHLORIC ACID

For the manufacture of bleaching powder, by the absorption of chlorine gas in slaked lime, large quantities of chlorine are annually consumed, and consequently the economical production of chlorine becomes one of the serious problems confronting the alkali industry in its course of development.

In 1823 the Leblanc soda process was introduced into England by Muspratt. At first the hydrochloric acid resulting from the salt-cake process was turned into the air, but, owing to the pressure of the Alkali Acts of 1863 and 1874, as well as the serious competition of the Solvay ammonia soda process introduced in 1866, the utilisation of hydrochloric acid in the most profitable manner became necessary to ensure the financial stability of the older Leblanc process. With the increasing extension of electrolytic methods for the production of soda from salt and the displacement of bleaching powder by liquid chlorine in the industries, it appears possible that the final development of these processes has now been reached.

The Deacon process.—The possibilities inherent in the oxidation of hydrochloric acid by means of atmospheric oxygen attracted the attention of inventors at a very early date, notably Oxland in 1840, Vogel and Thibierge in 1855 and Binks in 1860. It was not, however, until 1868 that H. Deacon and F. Hurter established the process as a satisfactory technical industry.

In its earliest form the hydrochloric acid from the salt-cake pans was mixed with four volumes of air and passed through iron superheaters to the contact chambers. The contact chambers or decomposing towers were iron cylinders about 12 feet wide filled with broken clay brick impregnated with cuprous chloride (Fig. 11) (the brick containing from 0·6 to 0·7 per cent. of metallic copper) maintained at 500° by the waste heat from the superheaters. About two-thirds of the hydrochloric acid was found to be oxidised according to the equation:

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

Condensation of the steam and unchanged hydrochloric acid was effected by earthenware pipes, whilst the residual 5 per cent. to 10 per cent. of chlorine gas was dried in sulphuric acid prior to absorption in slaked lime.

Several technical difficulties were inherent in the earlier plants, notably the loss of most of the "pan acid" and all the "roaster acid" from the Leblanc process, the impossibility of obtaining a continuous supply of gas, the rapid poisoning of the catalyst, and the very indifferent yields obtained.

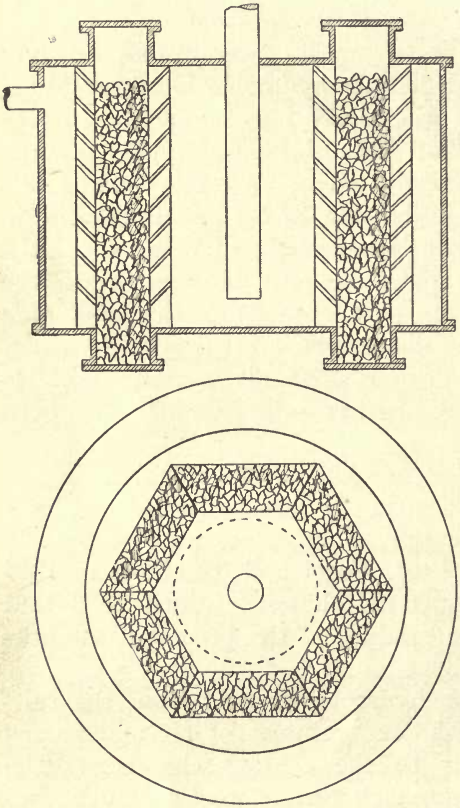

Fig. 11.

Hasenclever, in 1883, introduced the method of purifying the hydrochloric acid by absorption in water and blowing the purified gas out again by air in the presence of sulphuric acid. A sulphuric acid drier for the gases prior to passage through the superheater was simultaneously introduced. By this method a continuous supply of pure gases free from poisons such as sulphuric acid, $FeCl_2$,SO_2,As_2O_3, and carbon dioxide was thus obtained. The life of the catalyst was extended to from ten to twelve weeks and more than 12 tons of bleaching powder could be prepared with the loss of only 1 ton of impregnated clay. Subsequent improvements in the yield were made as a result of the investigations of J. H.

Harker,[1] Lunge and Marmier,[2] G. N. Lewis,[3] and Vogel v. Falckenstein.[4]

It was evident that the process involved the partition of hydrogen between oxygen and chlorine, the reaction

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

being strictly reversible. Also the function of the cuprous chloride was shown to be purely catalytic in establishing the equilibrium at the temperature of operation.

The values of the equilibrium constant $K = \frac{C^2_{H_2O} \cdot C_{Cl_2}{}^2}{C^4_{HCl} \cdot C_{O_2}}$ at different temperatures were investigated, using the dynamic method by von Falckenstein, who passed different gas mixtures of the four constituents over cupric chloride and platinic chloride catalysts, maintained at suitable temperatures in an electric furnace. G. N. Lewis utilised the static method, obtaining equilibrium when commencing with mixtures of hydrochloric acid and oxygen.

The following results were obtained :—

Temperature.	log K.
352°	2·43
356	1·90
419	1·52
450	1·40
600	0
650	−0·4

If the heat of reaction Q (13,800 calories) be assumed to be independent of the temperature, Lewis showed that the values of K at various temperatures could be calculated from the following equation :

$$\log_{10} K = \frac{6036}{T} - 7{\cdot}244.$$

The reaction may, of course, be considered as the combination of two simpler reactions :

$$2H_2O \rightleftarrows 2H_2 + O_2$$
$$2HCl \rightarrow H_2 + Cl_2$$

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[1] *Zeitsch. physikal. Chem.*, 1892, **9**, 673.

[2] *Zeitsch. angew. Chem.*, 1897, 108.

[3] *J. Amer. Chem. Soc.*, 1906, **28**, 1380.

[4] *Zeitsch. physikal. Chem.*, 1909, **65**, 371.

$$\text{if } K_1 = \frac{p^2_{H_2} \cdot p_{O_2}}{p^2_{H_2O}} \text{ and } K_2 = \frac{p_{H_2} \cdot p_{Cl_2}}{p^2_{HCl}},$$

$$\text{then } \log_{10} K = 2 \log_{10} K_2 - \log_{10} K_1$$

Adopting Nernst and Wartenberg's figures for the dissociation of water vapour at high temperatures,

$$\log_{10} K_1 = \frac{25050}{T} + 1{\cdot}75 \log_{10} T + 0{\cdot}00028\, T - 0{\cdot}2,$$

and employing for K_2 the value from the corresponding investigations of Dolezalek and Lowenstein on the dissociation of hydrochloric acid :

$$\log_{10} K_2 = -\frac{9626}{T} - 0{\cdot}8,$$

it follows that

$$\log_{10} K = \frac{5790}{T} - 1{\cdot}75 \log T - 0{\cdot}00028\, T - 1{\cdot}4.$$

Either of the above equations gives values of K which approximate very closely to the observed values. Nernst[1] gives the following calculated values, in close agreement with the determinations of v. Falckenstein :

Temperature.	log T.
450°	1·50
600	−0·009
650	−0·430

The fractional conversion of hydrochloric acid in dry air into chlorine can be calculated in a similar manner to that detailed in the oxidation of sulphur dioxide by the contact process. If x be the percentage of the hydrochloric acid it is easily seen that :

$$\sqrt[4]{K} = \frac{C^{\frac{1}{2}}_{H_2O} \cdot C^{\frac{1}{2}}_{Cl_2}}{C_{HCl} \cdot C^{\frac{1}{4}}_{O_2}} = \frac{x}{2(1-x)C^{\frac{1}{4}}_{O_2}}.$$

Excess of oxygen is thus beneficial to the yield of chlorine, but the conversion is not appreciably affected by slight alterations in the air supply owing to the dependence of the equilibrium on the fourth root of the oxygen pressure only.

The increase in the values of K with decrease in temperature

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[1] "Application of Thermodynamics to Chemistry," 89.

pointed to the necessity of finding suitable catalytic material for increasing the reaction velocity at low temperatures. No catalyst has as yet been found superior or even equal to Hurter and Deacon's cuprous chloride. With pumice impregnated with cuprous chloride Lunge and Marmier found that catalysis was already commencing at 310°, but the reaction velocity was still very slow below 400°. At 450—460° the reaction velocity is sufficiently rapid to give a satisfactory yield under technical working conditions.

Hurter suggested the use of cuprous chloride from a survey of the heats of formation of the chlorides and oxides of the various elements, showing that no other element except copper formed oxides and chlorides in which the combination was of so loose a character.[1] The mechanism of the reaction according to Deacon is based on the following cycle :

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$
$$Cu_2Cl_2 + O = CuO{\cdot}CuCl_2$$
$$Cu_2Cl_2O + 2HCl = 2CuCl_2 + H_2O$$

Levi and Bettoni as the result of a series of experiments with various catalysts,[2] such as $CuCl_2$, $CuSO_4$, $MnCl_2$, $MgCl_2$ and hot pumice, arrived at the conclusion that the extraction of water was the chief function of the catalyst, and that temporary hydrate formation played an important *rôle* in the process :

$$CuSO_4 + 2HCl + O_2 = CuSO_4,H_2O + Cl_2$$
$$CuSO_4,H_2O = CuSO_4 + H_2O.$$

Subsequently, the oxychloride, $CuO{\cdot}CuCl_2$, was isolated and the original views of Deacon and Hurter received further support in the discovery that most substances capable of forming oxychlorides were catalytically active.

V. Falckenstein drew attention to the necessity of carefully drying the gases before catalysis, and he showed that if the effluent gases were dried by sulphuric acid and again passed through the catalyst the conversion would rise from 82·5 to 85 per cent. and on a further passage to 88 per cent., owing to the shifting of the equilibrium ratio, $\frac{HCl}{Cl_2}$, by the abstraction of the water formed during the reaction.

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[1] *J. Soc. Chem. Ind.*, 1883, **2**, 106.

[2] *Gazzetta*, 1905, **351**, 320.

The two technical difficulties associated with the use of cuprous chloride as a catalyst are its sensitiveness to poisons and its volatility at the lowest working temperature, 450°.

Hasenclever's method of purification of the hydrochloric acid effects a very considerable improvement in the purity of the gas, but sulphur dioxide, as well as sulphuric acid spray, are not entirely eliminated. Kolb, in 1891, suggested the further purification by passage over hot salt maintained at 450°, whereby sodium sulphate was formed, and a small additional quantity of hydrochloric acid would pass on with the main gas stream.

Less volatile but more inefficient catalysts than cuprous chloride have been proposed from time to time, but owing to the bad yields resulting from the higher temperatures employed they have not found technical application.

Amongst the more important may be mentioned: ferric chloride, suggested by Thibierge in 1855, and platinised asbestos, by Weldon 1871. Hargreaves and Robinson (1872) suggested chromic oxide, De Wilde and Reychler,[1] mixtures of manganese and magnesium chlorides, in which a complex oxide was assumed to be an intermediary in the cycle of reactions:

$$3MgCl_2 + 3MnCl_2 + 4O_2 = Mn_3Mg_3O_8 + 6Cl_2$$
$$Mn_3Mg_3O_8 + 16HCl = 3MgCl_2 + 3MnCl_2 + 8H_2O + 2Cl_2.$$

Ditz and Margosches, in 1904, employed the chlorides of the rare earths, whilst Dieffenbach, in 1908, suggested the double chlorides of copper and other elements.

Mond[2] put forward a somewhat ingenious scheme to obtain more concentrated chlorine gas than that obtained in the usual Deacon process. If air and hydrochloric acid be passed alternately over heated nickel oxide deposited on pumice, the oxidation of the hydrochloric acid can be made a two-stage process through the intermediary formation of nickel chloride, which is reconverted into the oxide by the air. The idea does not seem to have been developed.

The Weldon process.—In 1869, W. Weldon introduced, at St. Helens, a process for the oxidation of hydrochloric acid in solution. At one time the process had a very considerable

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[1] B.P. 17272/1889.

[2] B.P. 8308/1886.

industrial importance, but is now being supplanted by modifications of the Deacon process already described.

Weldon's process suffers from the disadvantage that nearly 60 per cent. of the original hydrochloric acid is lost in the form of calcium chloride, in addition to 3 per cent. by weight, on the chlorine obtained, of the catalyst, manganese dioxide (pyrolusite); but, its development was doubtless due to the great advantage it possessed over the Deacon process, in that the chlorine gas evolved was very concentrated. The method of technical operation is as follows: hydrochloric acid, approximately 30 per cent. strength, is first oxidised by means of manganese dioxide:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The spent manganese chloride solution is then carefully neutralised with limestone, and after removal of any ferric hydroxide by precipitation is made alkaline by the addition of milk of lime, 30 per cent. in excess of that required to precipitate all the manganous hydroxide being added:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

The Weldon "mud" is now aerated at 50—60° for several hours, calcium manganate being finally precipitated:

$$2Mn(OH)_2 + O_2 + Ca(OH)_2 = CaO{\cdot}2MnO_2 + 3H_2O.$$

On the addition of more manganous chloride and lime during the process of aeration, a further oxidation ensues:

$$2CaO{\cdot}MnO_2 + 2Ca(OH)_2 + 2MnCl_2 + O_2 = 2(CaO{\cdot}2MnO_2) + 2CaCl_2 + 2H_2O.$$

It will be noted that when the regenerated manganese dioxide is used for the oxidation of a fresh quantity of hydrochloric acid a very considerable quantity of free base has first to be neutralised, thus again lowering the conversion efficiency of the process.

The mechanism of the process depends essentially on the use of the manganese salt as an oxygen carrier. Although we can show from the previous considerations in the Deacon process that atmospheric oxygen should be able to displace the chlorine from even weak solutions of hydrochloric acid, no active catalyst for this reaction has yet been found. If we extrapolate from v. Falckenstein's figures, the probable value of $K = \frac{[H_2O][Cl_2]}{[HCl]^2[O_2]^{1/2}}$ at 0°, we obtain a value of $K = 10^7$. The solubility of chlorine gas under 1 atmosphere is about 1 gram per litre, and of oxygen under two-fifths of an atmosphere 0·007 gram per litre, or $\frac{[Cl_2]}{[O_2]^{1/2}}$ in a liquid saturated with both gases at the respective pressures $= \frac{1}{0 \cdot 005}$ approximately.

Hence $\frac{[H_2O]}{[HCl]^2} = 10^7 \times 0 \cdot 085 = \text{Ca } 10^6$.

That is to say, the dilution below which atmospheric oxygen would be inoperative in displacing chlorine from hydrochloric acid is remarkably small.

Weldon relied upon the preparation of a more active oxidising agent than atmospheric oxygen, so that the oxidation of the acid might proceed at reasonable velocities. The method by which the oxidising power or oxidising potential of atmospheric oxygen is raised above its normal value at the expense of the energy lost in the combination of the acid with the free alkali is an interesting one.

We may write the oxidation reaction as follows :

$$MnO_2 + 2H_2O \rightleftarrows Mn(OH)_2 + 2(OH)' + 2\oplus \rightleftarrows$$
$$Mn^{\cdot\cdot} + 2(OH)' + 2(OH)' + 2\oplus .$$

The potential difference between an (MnO_2) electrode immersed in the Weldon mud and the solution itself is given by the equation :

$$E = E_0 + \frac{RT}{2\epsilon}\log\frac{[MnO_2][H_2O]^2}{[Mn^{\cdot\cdot}][OH']^4} = E'_0 + \frac{RT}{2\epsilon}\log K\frac{H^{\cdot 4}}{Mn^{\cdot\cdot}},$$

since $[MnO_2]$ and $[H_2O]$ can be assumed to be constant.

If this electrode be coupled up with an auxiliary oxygen electrode in a neutral solution, neglecting the P.D. at the boundary of the Weldon mud and the electrolyte surrounding the oxygen electrode, the E.M.F. of the cell thus set up is obtainable from the following relationship :

$$\mathrm{PtO_2}\ \underset{\underset{E_1}{\downarrow}}{\Big|}\ \mathrm{Mn(OH)_2}\ \underset{\underset{E_2}{\downarrow}}{\Big|}\ \mathrm{MnO_2Pt}$$

$$V = E_1 - E_2 = E_0 + \frac{RT}{2\epsilon}\log\frac{C_{O''}}{\sqrt{p_{O2}}} - E'_0 - \frac{RT}{2\epsilon}\log\frac{H^{\cdot 4}}{Mn^{\cdot\cdot}}.$$

The value of E_0 is approximately 1·22 volts, taking p as 1 atmosphere and a neutral electrolyte.

The value for E'_0 can be obtained from the investigations of Tower,[1] Inglis[2] and Haehnel,[3] and may be taken as equal to the value $E'_0 = 1{\cdot}35$ volts.

Hence :

$$E_1 - E_2 = 1{\cdot}22 - 1{\cdot}35 + \frac{RT}{2\epsilon}\left(\log H^{\cdot 2} - \log\frac{H^{\cdot 4}}{Mn^{\cdot\cdot}}\right)$$

$$= -0{\cdot}13 + \frac{RT}{2\epsilon}\log\frac{Mn^{\cdot\cdot}}{H^{\cdot 2}} = -0{\cdot}13 + \frac{RT}{2\epsilon}\log Mn^{\cdot\cdot}(OH')^2\cdot\frac{1}{c^2}.$$

where c is the value of the product $C_{H^\cdot}\ C_{OH'} = C_{H^\cdot}{}^2$ in pure water.

In a neutral solution, the solubility coefficient $Mn^{\cdot\cdot}(OH')^2 = 4 \times 10^{-14}$ approximately.

Hence :

$$E_1 - E_2 = -0{\cdot}13 + 0{\cdot}029\log\frac{4 \times 10^{-14}}{(0{\cdot}5 \times 10^{-14})^2}$$

$$= -0{\cdot}13 + 0{\cdot}45 = 0{\cdot}32 \text{ volt.}$$

In a similar manner, we can calculate the P.D. of the cell in normal hydrion concentration and with a normal $Mn^{\cdot\cdot}$ concentration.

$$V = -0{\cdot}13 + \frac{RT}{2\epsilon}\log Mn^{\cdot\cdot} - \frac{RT}{2\epsilon} \times 2\log H^{\cdot} = -0{\cdot}13.$$

For a normal $Mn^{\cdot\cdot\cdot\cdot}$ concentration the P.D. would obviously be much greater.

Thus in acid solutions the oxidising potential of the MnO_2 electrode exceeds that of atmospheric oxygen and necessarily

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[1] *Zeitsch. physikal. Chem.*, 1895, **18**, 17, 18.

[2] *Zeitsch. Elektrochem.*, 1903, **99**, 226.

[3] *Ibid.*, 1909, **15**, 834.

that of chlorine, since in *n*-hydrion concentration the cell, $PtO_2 | Cl_2 | Pt$, has an E.M.F.

$$V_1 = V_0 + \frac{RT}{2\epsilon} \log \frac{p_O'' \; p_{Cl_2}}{\sqrt{p_{O2}} \; (p_{Cl'})^2} = 1{\cdot}493 - 1{\cdot}35 = 0{\cdot}14 \text{ volt.}$$

indicating that the manganese "mud" has an oxidising potential at least 0·27 volt higher than the liberated chlorine, thus giving a measure of the energy available for oxidation of the hydrochloric acid. In neutral solutions the manganese "mud" possesses an oxidising potential inferior to that of oxygen or of chlorine.

In actual practice, more alkali has to be added than is necessary to ensure the oxidation of the manganous salt. In the early experiments of Weldon, red solutions were occasionally obtained during the process of oxidation, and it was found that the quantity of manganese dioxide formed during aeration was very small. It was finally shown that the red colour was due to the formation of manganous manganic oxide, owing to a deficiency of base according to the interaction:

$$MnO_2 + \tfrac{1}{2}H_2O \rightleftarrows \tfrac{1}{2}Mn_2O_3 + OH' + \oplus,$$

where

$$E = E_0 + \frac{RT}{\epsilon} \log \frac{(MnO_2)(H_2O)^{\frac{1}{2}}}{(Mn_2O_3)^{\frac{1}{2}}(OH')}$$

or

$$E = E_0 + \frac{RT}{\epsilon} \log C \frac{H^{\cdot}}{Mn^{\cdots}}.$$

Manganous manganic oxide is not easily decomposed by the addition of more alkali and subsequent aeration, so that in practice the red or "foxy" batches are passed straight to the stills to recover as much acid as possible before starting *de novo*.

Other processes for the oxidation of hydrochloric acid.—Owing to the inefficiency of the Weldon process from the yield point of view, the inventor and Péchiney experimented for many years on the production of chlorine by the aid of the following cyclic process:

$$4\,MgCl_2 + 2H_2O + O_2 = 4MgO + 4HCl + 2Cl_2$$
$$MgO + 2HCl = MgCl_2 + H_2O.$$

A pure magnesium chloride was not utilised, but the crude liquor after evaporation was mixed with the required amount of powdered magnesia to form the oxychloride, $MgO{\cdot}MgCl_2$, prior to drying at 300°. The chlorine and hydrochloric acid together with some steam were removed by an air blast at 1000°.

Another ingenious process which has been the subject matter of various patents involves the following cyclic process in which oxides of nitrogen play the part of catalysts, as in the sulphuric acid lead chamber process.

$$\begin{aligned} 3HCl + HNO_3 &= Cl_2 + NOCl + 2H_2O \\ HNO_3 + NOCl &= N_2O_4 + HCl \\ N_2O_4 + 2HCl &= N_2O_3 + H_2O + Cl_2 \\ N_2O_3 + O_2 + H_2O &= 2HNO_3. \end{aligned}$$

This idea, developed by Dunlop in 1849, together with the Weldon-Péchiney process outlined above, does not appear to have received any considerable technical development.

THE FRACTIONAL COMBUSTION OF HYDROGEN SULPHIDE

We have already indicated the technical significance of the catalytic processes employed for the oxidation of sulphur dioxide to sulphuric anhydride. A great part of the dioxide utilised for this purpose is derived from the combustion of natural sulphides, especially pyrites and blende, or from artificial sulphides such as gas-works spent oxide, yet a certain quantity is always obtained from the combustion of elementary sulphur. In 1882, Claus introduced a method for the fractional combustion of hydrogen sulphide into sulphur and water, thus preparing sulphuric acid by a three-stage process.

$$\begin{aligned} (1)\ 2H_2S + O_2 &= 2H_2O + 2S \\ (2)\ 2S + 2O_2 &= 2SO_2 \\ (3)\ 2SO_2 + O_2 + H_2O &= H_2SO_4. \end{aligned}$$

It has been suggested that the combustion of hydrogen sulphide to sulphur dioxide could be accomplished in one stage which, in the presence of excess of air, could be used directly for the preparation of sulphuric acid. This idea does not seem to have received any technical development, chiefly on account of the very large quantities of diluent nitrogen present in the resulting sulphur dioxide gas mixture.

The Claus process, however, in the hands of A. M. Chance, has been developed, and at the present time is the most satisfactory method of dealing with the alkali waste of the Leblanc soda process.

Alkali waste contains some 40 per cent. of calcium sulphide, 20 per cent. of calcium carbonate, and 10 per cent. of lime, the residue consisting chiefly of silicates with small quantities of sodium carbonate and iron sulphide. Chance modified Gossage's (1838) process for the production of a gas rich in sulphuretted hydrogen by decomposition with carbon dioxide. Carbon dioxide from lime-kilns is passed through a set of carbonating towers through which a suspension of alkali waste flows in the counter-current direction. In the first tower sulphuretted hydrogen is evolved according to the equation :

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S.$$

The hydrogen sulphide diluted with the nitrogen in the original kiln gas passes to the second tower, in which the hydrogen sulphide is absorbed, with the formation of calcium hydrosulphide :

$$CaS + H_2S = H_2CaS_2.$$

On carbonating this solution a gas containing twice as much hydrogen sulphide as was obtained from the first tower is evolved and collected in gas-holders over water covered with a layer of oil.

The sulphuretted hydrogen thus obtained, of about 38 per cent. purity, is mixed with air in the proportion of 5 volumes of gas to 4 volumes of air and passed into the Claus kiln for fractional combustion into sulphur and water vapour.

The Claus kiln consists essentially of a fire-brick cylinder containing a grating on which the catalytic material, usually bog iron ore (hydrated ferric oxide ignited at a low temperature), is deposited. The combustion is started by throwing a little red-hot coal into the furnace and is maintained by the heat of the reaction itself. The temperature of the eflowing gases, one foot from the kiln, should not exceed 300°, otherwise a loss of sulphur occurs. The hot gases are subsequently passed into a series of condensing chambers, where part of the sulphur condenses to the liquid state and the rest is recovered as flowers of sulphur in the condensed steam.

In order to minimise the loss of sulphur compounds (H_2S or SO_2) in the effluent gases, the exact theoretical ratio, $H_2S : O_2$, required for combustion in the entering gases must be maintained. The temperature of the catalyst is mainly determined by the speed of passage of the gas.[1]

Various other catalytic materials for this combustion process have been utilised, such as broken fire-brick, bauxite, and dried Weldon mud. There are, however, two distinct advantages in making use of an active catalyst which will operate at low temperatures. First, the life of the kiln and the condensing chambers is considerably shortened by high temperature operation, and, secondly, above 200° an interesting reverse reaction between the sulphur and the steam formed begins to take place with appreciable velocity :

$$2H_2O + 3S \rightleftarrows 2H_2S + SO_2.$$

It is extremely probable that the flowers of sulphur recovered in the condensed water do not originate in the original condensate of sulphur vapour from the combustion process, but result from the interaction in solution of the sulphur dioxide and hydrogen sulphide formed in the lower parts of the kiln and in those condensers which are above 100° to 200°.

The catalytic activity of oxides of iron and manganese in the Claus process is usually attributed to the property these elements have of forming more than one oxide, thus permitting the assumption of an oscillating oxide acting as oxygen carrier

$$\begin{tikzcd}
Fe_2O_3 \arrow[d] & O_2 \arrow[l] \arrow[r] & O_3Fe_2 \arrow[d] \\
H_2S \arrow[r] & Fe_2O_2 \arrow[u] & H_2S. \arrow[l]
\end{tikzcd}$$

Some experiments by the writers, however, indicate that iron sulphide is an intermediary compound in the process of

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[1] See, however, Carpenter and Linder, *J. Soc. Chem. Ind.*, 1903, **22**, 457 ; 1904, **23**, 557.

oxidation, and that the mechanism of oxidation can be more truly represented on the following lines, making the Claus process simply an extension of the ordinary gas-works process of spent oxide revivification (see p. 113).

$$Fe_2O_3 + 3H_2S \rightleftarrows 2FeS + 3H_2O + S$$
$$4FeS + 3O_2 \rightleftarrows 2FeO + 4S.$$

CATALYSIS IN THE PURIFICATION OF ILLUMINATING GAS AND GASEOUS FUELS

As is well known, illuminating gas after leaving the scrubbers contains various quantities of substances which are deleterious in the uses to which the gas is subsequently put. Thus, in addition to substances like carbon dioxide, which lower the illuminating power and calorific value of the product, the scrubbed gas may contain anything from 0·5 to 2·0 per cent. of sulphuretted hydrogen as well as organically combined sulphur compounds, such as carbon disulphide, thiophene, and mercaptans, to the extent of 10 to 80 grains of sulphur per 100 cubic feet of gas. Such sulphur compounds, since, on combustion, they yield sulphur dioxide, are disagreeable constituents of the final product. Their removal is consequently desirable. Indeed, the removal of free sulphuretted hydrogen is required by statutory regulation. Formerly, also, the removal of the combined sulphur to a certain degree was also required by statute, but this is no longer required.

In practice it is the custom to free illuminating and other gases from sulphuretted hydrogen by passing them through various suitably moistened absorbent materials, among which the more commonly employed are lime, oxide of iron, and manganese dioxide in the form of Weldon mud. The former removes both carbon dioxide and the sulphuretted hydrogen, together with a fraction of the carbon disulphide present. Its use, however, is becoming more and more restricted, especially to small undertakings having a local market for the product, since the disposal of the spent lime, containing both carbonate and a sludge of calcium sulphide, is both difficult and disagreeable, owing to the obnoxious odour which the material possesses. The oxides of iron and manganese are increasingly used and in a manner which involves their functioning as catalysts.

The elimination of sulphuretted hydrogen by means of oxide of iron is carried out in huge boxes carrying the absorbent material. This is generally employed in the form of bog iron ore which, from its content of organic matter, is porous and thus favours ready transformation to sulphide. If the precipitated hydroxide be employed, the material is generally lightened by admixture with organic matter in the form of sawdust. The material is at all times kept suitably moist. Absorption of the sulphuretted hydrogen involves a change of the absorbent from the brownish hydrated oxide to the blackish-green sulphide. Ferric sulphide and ferrous sulphide and sulphur are the products of the transformation, which may be symbolised by the equations :

$$Fe_2O_3 + H_2O + 3H_2S = Fe_2S_3 + 4H_2O$$
$$Fe_2O_3 + H_2O + 3H_2S = 2FeS + S + 4H_2O.$$

After absorption ceases, the sulphides, by exposure to air, may be transformed into the original material with the simultaneous production of sulphur, which change may be represented by the equations :

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S$$
$$4FeS + 3O_2 = 2Fe_2O_3 + 4S.$$

Thus, by alternation of the process of absorption and of exposure to air, or revivification, the original oxide of iron may effect the catalytic conversion of the sulphuretted hydrogen to sulphur and thereby the removal of the sulphur from the gas. As much as 50 per cent. of sulphur may thus be accumulated in the oxide by alternation of the two stages, and the resultant material is then a convenient source of sulphur for sulphuric acid manufacture.

In actual operation under working conditions, illuminating gas generally contains small amounts of oxygen entering the gas through leakages in the system. This oxygen effects, to a certain degree, in the boxes, the process of revivification attained otherwise by exposure to air. The observation of this action of oxygen has led to a development of modern gas purification in which the oxygen content of the gas at the entrance to the oxide purification system is controlled, and, if necessary, air is added to the gas to be purified to facilitate the process of revivification *in situ.* Thus, the process of purification becomes in essence the catalytic conversion, by means of oxide of iron acting as catalyst, of sulphuretted hydrogen and oxygen to sulphur and water according to the equation :

$$2H_2S + O_2 = 2H_2O + 2S + 110{,}000 \text{ cal.}$$

The advantage to be obtained from the admission of air to the purification system is that the purifiers can be worked for much longer periods without recharging. In modern gas-works practice this period may amount to as much as six months per box with a system of purification employing four boxes in series. The amount of oxygen added is restricted by two factors, the diluent effect on the gas of the nitrogen simultaneously added and the fact that the heat effect of the reaction may be so great locally as to cause combustion of the material in the purifiers with consequent introduction of sulphur dioxide into the gas and disorganisation of the purification system. The care requisite in this regard will readily be appreciated by the gas engineer who has knowledge of the strongly exothermic nature of the reaction, which, as given in the equation above, amounts to 110,000 cal.

Precipitated oxide of iron, an artificially prepared material, has come into considerable use as the catalytic material, since its action is found to be more vigorous than the natural bog iron ore. For similar reasons, the manganese dioxide of Weldon mud is also employed, its reactivity with sulphuretted hydrogen being computed to be five times that of the bog ore. All the materials are employed until so far loaded with sulphur that they are available as an economical source of sulphur.

It is to be pointed out that all the fuel gases of industry contain greater or less amounts of sulphuretted hydrogen, and are therefore potential sources of sulphur supply for the sulphuric acid industry. The gases from by-product coking ovens are also a further such source. Since, however, the capital outlay in plant and space for oxide box purification is considerable, the economy of the purification process is small, and these sources of sulphur have to a marked degree been neglected, the sulphur being left in the gas with consequent vitiation of the atmosphere in the neighbourhood of their combustion. It is to be hoped that further improvement may be effected in the recovery of sulphuretted hydrogen from all fuel gases so as to render its removal a sound economic proposition and thereby minimise the dependence of the community for sulphur upon foreign sources of supply.

The elimination of sulphuretted hydrogen from coal-gas by the methods just outlined is remarkably complete, and with skilled supervision the quantities of such gas in modern illuminating gas are negligible. The process, however, except when lime is employed, fails to bring about the removal of the organically combined sulphur compounds, and, in the case of lime, only partial removal of carbon disulphide is effected. Attempts to eliminate organically combined sulphur are almost as old as the illuminating gas industry itself, and as many of the suggested processes are catalytic in nature their record is essential here.[1] So far back as 1806, Edward Heard suggested passing the crude gas over alkaline earth or certain metals or their oxides placed in iron tubes or other vessels and exposed to a furnace. In 1818, Palmer took out patents upon a process of removal by passage of the crude coal-gas through heated tubes containing iron, oxide of iron, or iron stone, so disposed as to present as large a surface as possible. In the 'fifties Thompson suggested a process to operate upon a technical scale, of which the principle is merely to pass the gas over lime heated to a dull red or much lower, or small pieces of brick or pumice-stone previously steeped in a solution of the chloride of platinum. Bowditch, in 1860, patented a process for removal of combined sulphur by passing the gas first freed from sulphuretted hydrogen in the ordinary manner through heated clay, oxide of iron, or lime, the temperature found most efficient being between 140° and 215°. In 1870, Vernon Harcourt proposed to decompose organic sulphur compounds by placing a mass of iron turnings or wire into the mouthpiece of each retort or by conducting the gas through heated tubes partially filled with suitable

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[1] "Purification of Gas by Heat," Carpenter.

surface-presenting material, and a trial was made in 1874 of the process suitably modified for technical operation. I. von Quaglio, in 1878, proposed the use of heated clay balls impregnated with the chloride of a metallic catalyst, or such metals themselves in powdered form.

All these processes are in reality suggestions for conducting readily by means of catalytic agents a reaction which may be illustrated best with reference to carbon disulphide by means of the equation :

$$CS_2+H_2=H_2S+C.$$

Upon the laboratory scale this is readily effected and forms the basis of the Harcourt test for such sulphur compounds. As actually operated in the test, the gas is passed through a heated flask containing platinised pumice. The disulphide is decomposed quantitatively, and the formation of sulphuretted hydrogen determined by means of a colour test.

The installation of such a process of purification upon a large technical scale for the purification of illuminating gas is due to Hall and Papst, of the Portland Gas and Coke Co., Oregon, U.S.A. The device patented by Hall for the purpose is composed of two heaters filled with chequer work as in a water-gas plant, and a generator from which they are heated internally and alternately by producer gas. Whilst the coal-gas is being treated for sulphur compounds in the one heater, the other is being heated up by the gas from the generator, and so continuity of purification is ensured. During 1909 as many as 817 million cubic feet of gas were heated in this way at an average cost stated to be ½d. per 1,000 cubic feet. The percentage reduction of combined sulphur in the gas throughout the year averaged 70 per cent., reducing the content from an average of 59 grains to 17 grains per 100 cubic feet. The temperatures employed were high (up to 900° is suggested), so that doubtless there would be an accompanying loss in illuminating power. The percentage reduction increased with increasing temperature, varying from 20 per cent. at 427° to 76 per cent. at 704°.

The work of Carpenter and Evans[1] in England upon similar

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[1] Carpenter, *J. Gas Lighting*, 1914, **126**, 928; Evans, *J. Soc. Chem. Ind.*, 1915, **34**, 9.

lines may now be detailed. A variety of catalytic materials for the decomposition of the organic sulphur by means of hydrogen were studied with a view to their application upon a practicable scale. Among such materials may be mentioned fire-brick, pumice, iron oxide, platinum, and nickel. Of the contact materials studied, pumice or fireclay impregnated with finely divided nickel was chosen as the most suitable, being the most active and not prohibitive in cost. After smaller scale experiments, a large-scale plant with a capacity of 1¾ million cubic feet per day was erected. This was later supplemented by a plant dealing with 10 million cubic feet per day in London and one at East Greenwich in five units, each unit capable of dealing with 3 million cubic feet of gas per day. The gas to be heated is previously freed from sulphuretted hydrogen in the usual way and passes through a system of preheaters and heat interchangers to the reaction chamber, maintained at 450°, at which temperature approximately 80 per cent. conversion of the sulphur compounds may be obtained. The heated gas leaving the reaction chamber flows through the heat exchangers in the contrary direction, and permits therefore of economy in the heat required to be added to the system. In the East Greenwich plant, the weight of metallic nickel employed is 1,321 lb., equivalent approximately to 1 lb. of metallic nickel per 10,000 cubic feet of gas per day. The daily consumption of coke for the same plant amounts to 5½ tons per day. Provision is made for regeneration of the catalytic material after a period of use. This is necessary owing to the deposition of carbon resulting from the reaction in the catalytic material employed. Regeneration is effected by blowing hot air through the system, which burns off the carbon deposit from the fireclay ball impregnated with nickel. The average reduction of sulphur content in the 10 million cubic feet per day plant over a period of sixteen months was from 40 to 8 grains per 100 cubic feet or a percentage reduction amounting to 80 per cent. The effective reduction is to a certain degree governed by the sulphur content of the gas, a maximum reduction, equivalent to 84 per cent., being observed on a gas of 64 grains of sulphur per 100 cubic feet, the minimum being 72 per cent. on a gas of 19 grains sulphur content. The effect of the process on the illuminating power of a rich 20 candle-power gas was specially studied. It was found that the illuminating power was unimpaired, the average quality before and after treatment for sulphur being 20·54 and 20·46 candles respectively. The cost of working the sulphur extraction process is given as 0·3d. per 1,000 cubic feet, including fuel, maintenance charges, depreciation, and interest. The capital cost works out at £1,500 per million cubic feet of gas per day.

It is possible that yet another catalytic reaction may be employed technically, in the future, for removal of the combined sulphur from fuel and illuminating gases. It is well known that carbon disulphide reacts at suitable temperatures with water to form carbon dioxide and hydrogen sulphide, according to the equation :

$$CS_2+2H_2O=CO_2+2H_2S.$$

In a French process patented by Guillet,[1] this reaction is accelerated catalytically by means of oxide of iron maintained at temperatures between 80° and 300°. Reduction on a laboratory scale from 16 to 4·3 grains per 100 cubic feet was claimed at 130°.

The sulphuretted hydrogen formed is fixed, however, by the iron oxide, and hence the process, conducted in the above manner, must necessarily be discontinuous. On the other hand, it is known, for example, that in the catalytic hydrogen process employing water-gas and steam at 500° with iron oxide as basic catalytic material, all sulphur compounds are converted to hydrogen sulphide in the course of the reaction and pass on as such with the other products. It does not seem unlikely, therefore, that such a catalytic process for sulphide removal could be operated continuously if the right conditions were obtained. The reaction would possess a point of advantage over the processes previously considered, since carbon dioxide, and not carbon, is the product of conversion. The catalytic mass, therefore, would remain unaltered and the process of aeration requisite in the Hall and Papst, and in the Evans–Carpenter processes would be

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[1] *Soc. Tech. de l'Ind. du Gaz en France*, 1912, p. 245

unnecessary. Interesting technical developments of the process of M. Guillet may therefore be expected.

THE INFLUENCE OF CATALYSTS IN SURFACE COMBUSTION

During recent years, a considerable advance has been made in the technical application of the catalytic process of surface combustion by Schnabel in Germany, but more especially by Bone and his co-workers in England.[1]

In the preceding pages we have already discussed the catalytic activity of certain substances, notably platinum, in promoting the combination of oxygen and hydrogen as well as other combustible gaseous mixtures, and have noted that under suitable conditions the catalytic material can attain quite high temperatures. Thus Fletcher[2] appears to have been the first to study the conditions necessary to maintain the catalyst at a high temperature by the process of surface combustion. This investigator showed that it was possible by suitable regulation of the composition of a mixture of coal-gas and air to keep a ball of iron wire continuously at a high temperature without any combustion taking place in the form of flame, provided that the gaseous mixture came in direct contact with the hot material.

Bone, in 1902, commenced a systematic investigation on the influence of various catalytic materials such as platinum, gold, silver, copper and nickel oxides, and magnesia at fairly elevated temperatures, ca. 500°.

He noted that there was a steady increase in catalytic activity with elevation of the temperature and that the disparity between different catalytic materials diminished with ascending temperatures.

As a logical sequence to these earlier experiments, the conditions necessary for maintaining a catalytic material continuously and uniformly at a high temperature by surface combustion were developed.

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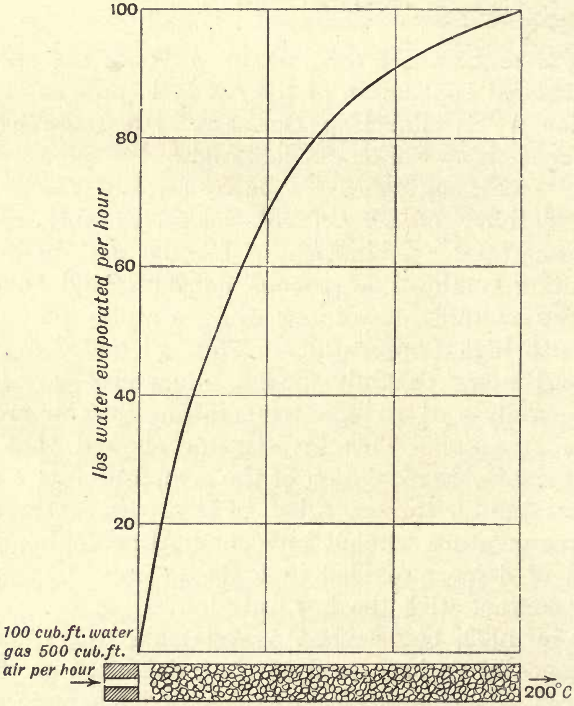
[1] *Phil. Trans.*, 1906, [*A*], 206; *Ber.*, 1913, **46**, 5; *Proc. Amer. Gas Inst.*, 1912, **6**, 564; R.I. Lecture, Feb., 1914.

[2] *J. Gas Lighting*, 1887, **1**, 168; see Bone, *loc. cit.*

Bone and McCourt's earliest types of apparatus consisted essentially of a porous fire-brick diaphragm through which a gas and air mixture in the correct ratio for complete combustion was forced by a suitable injector or blower. The fire-brick diaphragm rapidly attains a bright-red heat and complete combustion is effected in a very thin layer of the diaphragm ($\frac{1}{8}$ to $\frac{1}{4}$ inch). The advantages of such a heater, viz., the high efficiency in the production of effective radiant energy and the possibility of fixing the diaphragm in any position, are partly gainsaid by the necessity of using either air or gas under pressure, and by the fact that the diaphragms are slowly but continuously blocked up by dust and tar fog in the air or gas.



3 ft. unit heater for boiler, showing evaporation in lbs per foot

FIG. 12.

As a consequence, the surface combustion heater was modified by substituting a bed of refractory granular material for a diaphragm and forcing through it a suitable mixture of air and gas or vaporised fuel. Many applications of this method have given extremely successful results in practice. Thus the granular material may be packed round muffles, crucibles, or retorts or the flue tubes of steam boilers.

The following figures indicate the remarkable efficiency obtained when steam is raised by a gaseous fuel when this system of surface combustion is utilised :

Utilising a tube three feet long and three inches in internal diameter packed with granular refractory material as a heating unit, nearly 100 lb. of water could be evaporated per hour (20 to 22 lb. per square foot of heating surface) with 100 cubic feet of coal-gas and 550 cubic feet of air, representing an 88 per cent. transmission (to the water) of the net heat developed by the combustion (Fig. 12). This unit compared extremely favourably with the 50 per cent. obtained with blast furnace gas and the 65–70 per cent. obtained with coke-oven gas when the usual gas-firing systems are employed. It was noted that the effluent gas temperature was only 200° and in later experiments even this small amount of heat originally lost was utilised to heat up the boiler feed-water. Even better results were obtained with a large boiler erected at the Skinningrove Iron Works. This boiler, fitted with 110 heating units of the above-mentioned size, was capable of evaporating 5,000 lb. of water per hour with an average figure of 14·1 lb. per square foot of heating surface per hour, and on a ten-hour run gave the remarkably high figure of 92·7 per cent. efficiency. The efficiency of this boiler may be judged by the following figures :

Heat utilised	92·7	per cent.
Heat lost in burnt gases	3·0	,,
Heat lost by radiation	4·3	,,
	100·0	

Steam equivalent of power consumed by fan for driving the gases 2·7 per cent. Net over-all efficiency, 90·0 per cent.

More recent improvements in the "Bonecourt" boilers include a rigid system of refractory surfaces instead of a packing of granular material for dealing with gases liable to contain dust or tar fog and an increase in the size of the heating unit. Experimental trials[1] have shown that heating units up to 6 inches in diameter and from 13 to 21 feet long can be constructed without affecting the high rate of evaporation per square foot of heating surface.

THE INCANDESCENT MANTLE

The historical development of the incandescent gas mantle may be said to have commenced with the investigations of Drummond on the production of incandescent surfaces on certain refractories such as magnesia, lime, alumina, and zinc oxide by means of the oxy-hydrogen flame, whilst Berzelius first pointed out the uses of thoria and zirconia as light-emitting refractories. From 1839 to 1880, several inventors were exercising their ingenuity in the production of light from the Bunsen burner flame, amongst whom may be mentioned Cruickshank in 1839, Tessie du Motay in 1867, and Edison in 1878. It was not, however, until the period 1881–1883 that Williams, in New Jersey and Auer von Welsbach, in Vienna, practically simultaneously developed what is essentially the gas mantle of to-day.

The earlier mantles were made of cotton and possessed grave defects, such as shrinkage with use, resulting in crumbling; a twist in the fibre introduced in the spinning, making the mantle susceptible to shock, and, finally, a continuous diminution in light emissivity.

Present day mantles are generally made of artificial silk or grass cloth (ramie fibre) spun into threads.

It may be noted in passing that all varieties of artificial silk appear suitable for the manufacture of mantle material, including the silk from Swann and Chardonnet's collodion process, the more recent Cross and Bevan viscose and acetate methods, and Schweitzer's cupro-ammonium solvent.

Auer von Welsbach commenced his researches on the fractional crystallisation of the rarer elements in 1880, and during that year he noted that cotton threads could be

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[1] Bone, "Coal and its Scientific uses," Longmans, 1918.

impregnated so as to leave a coherent oxide ash as a skeleton. The colour of the flame produced on heating this skeleton in a Bunsen burner varied from yellow to green. In 1883 the earliest mantles were introduced, in which the oxides of zirconium and lanthanum were chiefly used, although the addition of smaller quantities of other oxides was simultaneously suggested.

In 1886, the use of thoria was patented[1] and the idea of strengthening the finished mantle for transport by immersion in collodion was also claimed.

None of these methods, however, proved satisfactory as far as life and light-emissivity were concerned, these being the two most important factors for technical success. From 1886 to 1891 Welsbach and his assistant Harbinger continued unsuccessfully their experiments upon the mantle, until an accidental observation that small quantities of ceria were always present in some specimens of thoria which possessed a somewhat higher emissivity than others, led to the introduction of the present day Welsbach mantle.

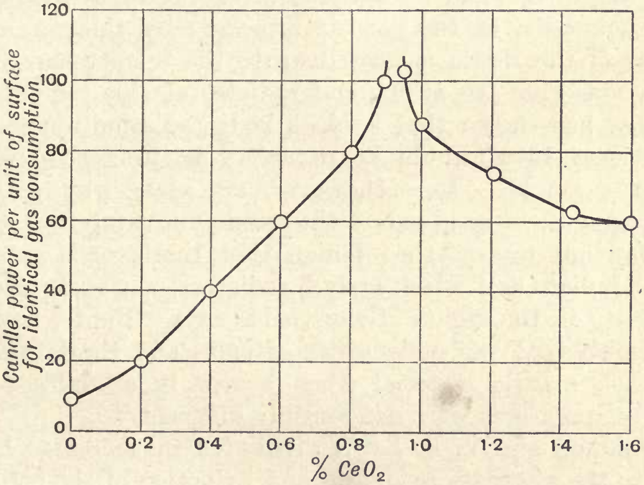

FIG. 13.

The extraordinary effect that small quantities of ceria may exert on the emissivity of thoria is indicated in the above curve (Fig. 13). It will be noted that the maximum emis-

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[1] D.R.P. 41945.

sivity is obtained when a 99·1 per cent. thoria—0·9 per cent. ceria mixture is utilised.[1]

Various theories have been put forward to explain the phenomenal increase in light emissivity in presence of ceria, but no satisfactory conclusion as to actual mechanism of light production has as yet been arrived at.

Westphal's theory that during the period of optimum emissivity the gradual combination of an acid oxide, *e.g.*, thoria, with a basic one such as ceria is taking place may be dismissed as untenable. Bunte's view is supported by a certain amount of experimental evidence. He regards the thoria as a heat-insulating surface and holds that the ceria catalytically hastens the combustion of the gas–air mixture; by this means the surface of the thoria is heated up to the temperature of the flame, viz. 1700° to 1870°, and radiates at this temperature. Rubens[2] has shown that a black body radiation temperature of at least 1600° would be necessary to produce a similar visible emissivity. It is, however, not clear why only 0·9 to 1 per cent. of ceria exerts the maximum catalytic activity. Le Chatelier was of the opinion that thoria–ceria mixtures do not radiate as "Black body" radiators, but exert selective emissivity in the region of the visible rays. Bunte, however, has shown that the emissivities of ceria and thoria and the Welsbach mantle material when heated in a muffle to the same temperatures were not sensibly different.

Wyrouboff and V. B. Lewis attributed the increased luminosity to the alternate oxidation and reduction of the ceria:

$$O_2 + 2Ce_2O_3 \rightleftarrows 4CeO_2,$$

the presence of 1 per cent. of ceria in the mixture being sufficient to ensure that combustion proceeds at its maximum velocity.

An important observation was made by Meyer and Anschütz,[3] who noted that CeO_2 forms a solid solution in thoria up to 7 per cent. and that a small quantity of CeO_3 was also present in a used mantle mixture. It is an interesting speculation as to whether the maximum dissociation of the cerium oxide in the thoria occurs in dilutions 0·9 to 1 per cent.

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[1] For a technical description of the manufacture of gas mantles, see R. Böhm, "Die Fabrikation der Gluhkörper für Gasglühlicht."

[2] *Ann. Physik*, 1906, **20**, 543.

[3] *Ber.*, 1907, **40**, 2639.

The loss of light emissivity with continued use is attributed by White and Müller[1] to the gradual volatilisation of the catalytic cerium oxide. Bruno,[2] on the other hand, considered that the cerium oxide became converted into an inert allotropic modification from which the active oxide could be regenerated by slowly cooling the mantle.

Various other substances have been used for the preparation of mantles, and it is interesting to note that the practice of adding an oxygen carrier is practically universal, thus lending colour to the suggestion of catalytic action of the ceria in the Welsbach mantle.

As catalytic oxygen carriers, chromium, vanadium, manganese, iron, cobalt, and even silver oxides, have been suggested. With the exception of the three first named, these oxides are much too volatile for practical use, unless retained on the mantle in the form of silicates, in which case their catalytic properties are considerably impaired. A composition of alumina and 8–16 parts of chromium oxide was largely used in the preparation of "Sunlight" mantles. With a thoria base, the following quantities of catalytic material are said to give roughly the same emissivity:

CeO_2,0·9–1·0 ; V_2O_5, 0·4 ; MnO_2, 1·5 ; U_3O_8, 0·25 per cent.

Other bases, in addition to thoria and alumina, have been suggested from time to time, such as, zirconia, magnesia, and lanthana-chalk mixtures. Magnesia has been shown to be rather volatile, whilst chalk suffers from the disadvantages of being readily attacked by water and carbon dioxide present in the air when the mantle is not in use.

Small quantities of the oxides of beryllium and aluminium are frequently added as hardeners in order to increase the resistant powers of the mantle.

THE PREPARATION OF FORMALDEHYDE

The earliest development of the formaldehyde industry was closely associated with its utilisation as a volatile disinfectant for rooms; for this purpose so-called formaldehyde

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[1] *J. Gas Lighting*, 1903, **83**, 504.

[2] *Zeitsch. f. Beleucht*, 1899, **5**, 244.

lamps were introduced in which methyl alcohol was caused to burn in specially constructed burners. A small fraction of the methyl alcohol was in this way converted into formaldehyde, but by far the greater portion was oxidised to carbon dioxide and steam according to the equations :

$$2CH_3{\cdot}OH + O_2 = 2H{\cdot}CHO + 2H_2O$$
$$2CH_3{\cdot}OH + 3O_2 = 2CO_2 + 4H_2O.$$

Modern room disinfection by means of formaldehyde is usually accomplished by the volatilisation of paraform $(H{\cdot}CHO)_3$ (Schering's formalin) in small lamps, or by chemical oxidation of methyl alcohol, by the use of permanganate[1] or barium peroxide (bleaching powder has also been suggested, Eischengrun's Autan method).

The earlier alcohol combustion lamps devised by Tollens, Bartel, Robinson, Trillat, Broche, Dieudonné, and others are no longer in use.

As new industrial uses for formaldehyde were found, notably in the hardening of gelatins, preservation of food, disinfection of hides, in certain leather tanning processes, as well as in the recent development of synthetic tannins, phenol formaldehyde condensation products for electrical insulator and other purposes (baekelite), and the fine organic chemical industry, the most suitable method of production on a technical scale became a matter of importance.

At the present time it may be stated that the only technical processes for the preparation of formaldehyde are those based on the fractional combustion of methyl alcohol ; but as will be subsequently shown these methods will probably be replaced by more economical catalytic processes which are still in the experimental state.

The earliest experimental work on the fractional combustion of methyl alcohol to formaldehyde dates from the time of Hofmann,[2] who obtained a small conversion by the passage of an air alcohol mixture through a red hot platinum tube. Gautier, as well as Tollens and Loew,[3] effected certain modifica-

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[1] Evans and Russell ; see Croner, "Disinfecktion" XI., 1909.

[2] *Ber.*, 1878, **11**, 1685.

[3] *Ibid.*, 1881, **14**, 2134 ; 1882, **15**, 1629, **20**, 141, *cf. J. pr. Chem.*, 1886, (ii), **33**, 321.

tions by substituting a glass tube packed with platinum or metallic copper foil as catalytic material; they laid stress on the influence of the presence of moisture in the original alcohol, the variability of yield with alteration in the oxygen alcohol ratio, and changes in the temperature of the catalyst. Trillat[1] in 1889 first proposed a large scale production plant in which crude methyl alcohol was evaporated, mixed with air and passed through the catalyst chamber containing platinum asbestos maintained at a dull red heat. Other catalytic materials such as copper oxide or even fire-brick were suggested. As a result of a series of experiments, Trillat was able to oxidise methyl alcohol with air by means of an electrically heated platinum gauze at 200°; with elevation of the temperature, decomposition proceeds further, as shown by the increase in the carbon monoxide and dioxide content. The optimum steam content for the methyl alcohol vapour was found to be in the neighbourhood of 20 per cent.

With oxidised copper gauze at 330°, Trillat obtained a 48·5 per cent. yield with an air alcohol ratio of 2·5 litres to 0·65 gram. In modern practice much higher temperatures are usually attained, *e.g.*, 450—550°.

Later, Sabatier and Mailhe[2] directed attention to Berthelot's experiments in which he showed that the thermal decomposition of primary alcohols in the absence of air was effected by two simultaneous reactions:

(*a*) A dehydration, *e.g.*, $C_2H_5{\cdot}OH \rightleftarrows CH_2{=}CH_2 + H_2O$,
(*b*) A dehydrogenation, $C_2H_5{\cdot}OH \leftrightarrows CH_3{\cdot}CHO + H_2$,

and proceeded to investigate the effect of various catalytic materials on these decompositions and showed that copper at a temperature of 200—300° was an effective dehydrogenation catalyst.

With freshly reduced copper oxide, the reduction proceeds according to the equation:

$$CH_3{\cdot}OH \leftrightarrows H{\cdot}CHO + H_2,$$

and the reaction is a reversible one, a 50 per cent. conversion

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[1] "Oxidation des Alcohols," 1901.

[2] See "La Catalyse en Chimie Organique" and *Ann. Chim. Phys.*, 1910, **20**, 344.

is obtained with a 5 per cent. loss of decomposition products and 45 per cent. unchanged methyl alcohol, which can be fractionated off and returned to the alcohol storage reservoir.

Unfortunately, in the case of methyl alcohol, copper appears rapidly to lose its activity; either owing to the gradual reduction of unchanged cuprous oxide in solid solution in the metal which may be the real effective catalytic agent or for some other cause as yet unknown. Consequently, experimenters have had recourse to elevation of the temperature to enhance the diminishing activity. At 300°, the second stage of the thermal decomposition into carbon monoxide and hydrogen is quite marked, whilst at 350° it is practically complete in presence of metallic copper at low space velocities :

$$H{\cdot}CHO = CO + H_2$$
$$\text{and } CH_3{\cdot}OH = CO + 2H_2$$

These reactions are also probably reversible in character and open up an interesting field for the future synthesis of methyl alcohol and formaldehyde. Sabatier and Senderens[1] investigated the catalytic activity of other metals and oxides on the dehydrogenation of methyl alcohol with the following results :

Substance.	Temperature commencement of dehydrogenation.	Temperature of maximum activity.	Loss of formaldehyde due to secondary decomposition.
Nickel	180°	360°	Above 60 per cent.
Cobalt	Slightly more active than nickel, but less than copper.		
Iron	Slightly less active than cobalt.		
Platinum	250°	—	Complete.
Manganese oxide	320	360°	Small.
SnO_2	260	350	Small, but reduction to metal takes place.
CdO	250	300	Complete.

The following catalytic oxides suitable for dehydrogenation of methyl alcohol in order of increasing activity are cited by Sabatier. The optimum temperature for dehydrogenation appears to be 350° :

$$GlO,\ SiO_2,\ TiO_2,\ ZnO,\ ZrO_2,\ MnO,\ Al_2O_3.$$

The use of bauxite for this purpose might possess certain advantages.

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[1] *Ann. Chim. Phys.*, 1905, 8, 4473.

It was therefore evident that the usual process of fractional combustion of methyl alcohol was actually based on the primary catalytic dehydrogenation of the alcohol into aldehyde and hydrogen, whilst the addition of oxygen might be regarded as necessary to maintain the temperature of the reaction (28 cal. being absorbed per gram-molecule in the dehydrogenation process), to lower the partial pressure of the hydrogen, and possibly to revivify the copper catalytic material by continuous alternate oxidation and reduction. E. I. Orloff[1] confirmed nearly all Sabatier's experiments, showing that the following catalysts were effective in the dehydrogenation process. Copper precipitated on asbestos, cerium sulphate and thorium oxide, platinum black, metallic platinum, coke containing precipitated copper, vanadium oxide on asbestos. Unsatisfactory results were obtained with iron, practically complete decomposition to oxides of carbon and lamp black occurring.

In his later communications Orloff advises the addition of air and recommends copper gauze preceded by platinised pumice or platinised asbestos, and states that the best conversion is effected when the reaction proceeds without the application of external energy and that the following relationships are obtained :

Ratio :
O_2 : MeOH : 0·4 : 1
Alcohol : Total volume gaseous mixture : 0·342 : 1

$$\frac{\text{Concentration of oxygen} \times \text{concentration of alcohol vapour}}{\text{Square of mean velocity of gas flow}} = 0{\cdot}00103.$$

Le Blanc and E. Plaschke[2] similarly conducted a series of experiments on fractional combustion of methyl alcohol, using silver wire gauze and electrolytically silvered copper gauze as catalysts ; they also arrived at the conclusion that the process is virtually one of dehydrogenation and that the function of the oxygen was merely to revivify the catalytic material, for which purpose freshly reduced copper was most suitable. Their most favourable yields were 58 per cent.

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[1] *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 855, 1023, 1414 ; 1908, **40**, 796.

[2] *Zeitsch. Elektrochem.*, 1911, **17**, 151.

with silver and 55·4 per cent. with copper, under the following experimental conditions :

Length of silver gauze spiral in cm.	Gram O_2 per gram alcohol.	Temp. of catalyst.	Velocity of air in litres per minute.
5·85	0·459	455°	2·669*

Per cent. conversion.	Per cent. unchanged.	Per cent. loss.	Diameter of tube.
58·06	26·43	15·51	30 mm.

* Representing a space velocity referred to the air of 3,900 (litres of air per litre of catalyst space per hour).

The effluent gas contained the following proportions of CO_2, CO and H_2 respectively 4·46, 4·16 and 11·49 per cent.

The figures represent the optimum yield obtained after alteration of all the independent variables one at a time.

Fokin[1] continued Orloff and Le Blanc's researches and obtained the following orders of activity for the conversion in the passage of alcohol air mixtures over different metals.

Ni	1·08 per cent.	Cu ..	43·47 per cent.
Al	1·5 ,,	Ag ..	64·60 ,,
Mn	2·01 ,,	Au ..	71 ,,
CO	2·8 ,,	CuAg alloy	84 ,,
Pt	5·2 ,,		

It will be noted that silver is extremely effective.

Bouliard[2] suggests the use of silver precipitated on flax as support material, whilst O. Blank[3] suggests silver on asbestos.

Hochstetter[4] has attempted to produce a catalytic material which should accelerate both reactions, viz., the dehydrogenation process, $CH_3{\cdot}OH = H{\cdot}CHO + H_2$, as well as the fractional combustion, $2CH_3{\cdot}OH + O_2 = H{\cdot}CHO + H_2O$. Thus, he states that he has obtained the following results by using metal couples instead of the pure metals.

	Per cent. yield.
Pure Cu	70
Cu alloyed with 1/10,000 Pt	72
Cu coated with 1/10,000 Pt	77
Ag	75
Ag with a Cu tube	84
Ag coated with 1/10,000 rhodium	96
Ag ,, ,, 1/10,000 Pt	96

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[1] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 286.

[2] F P. 412501/1910.

[3] *J. Soc. Chem. Ind.*, 1911, **30**, 49.

[4] B.P. 464/1914.

Other suggested methods of preparation of formaldehyde have been the subject of patent literature.

We have already observed that the reaction $H{\cdot}CHO = CO + H_2$ is probably a reversible one, and it is interesting to note that both the Badische[1] and Dreyfus[2] patents suggest passing a mixture of carbon monoxide and hydrogen in the ratio of 2 : 1 at 100 atmospheres pressure over catalytic materials (such as Pt, Cu, Fe, Cr, Ni, Ce, Ur, V, or their oxides) at 300°—400°.

Brodie,[3] Losanitsch and Jovitschitsch[4] obtained small quantities of formaldehyde from these gases when subjected to the silent electric discharge, Chapman and Holt,[5] by the high tension electric discharge, whilst de Jahn proved the presence of aldehyde when CO and H_2 were passed over spongy platinum into water.[6]

The thermal decomposition of dimethyl ether, tin formate,[7] and calcium formate, as well as the fractional reduction of formic acid by hydrogen over iron or nickel catalysts at 300° to 500°[8] are all suggested methods for the preparation of formaldehyde.

Equally interesting and worth attention are the various suggestions for the fractional combustion of methane into methyl alcohol or formaldehyde.

Glock,[9] in 1898, suggested the passage of a mixture of methane and air over granulated copper or pumice maintained at 800°, the process, being circulatory, removing the formaldehyde after each cycle by a system of scrubbers. Lance and Elsworthy[10] suggest the use of hydrogen peroxide or persulphuric acid as an oxidant in the presence of ferrous sulphate, presumably as a catalytic material. The Sauerstoff u. Stickstoff Ind.[11] and V. Unruh[12] claim the use of tan bark as catalyst, stating that oxidation of methane by air will take place at 30—50° in the presence of such material. It is more than probable that the aldehyde was itself derived

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[1] B.P. 20486/1913.

[2] B.P. 108855/1915.

[3] *Proc. Phys. Soc.*, 1874, **12**, 171.

[4] *Ber.*, 1897, **30**, 135.

[5] *J. Chem. Soc.*, 1905, **87**, 916.

[6] *Ber.*, 1889, **22**, 989.

[7] B.P. 183856.

[8] Badische Co. Pat. No. 185932.

[9] D.R.P. 107014. *See also* D.R.P. 286731.

[10] B.P. 7297/1916.

[11] D.R.P. 214155/1906.

[12] U.S. P. 891753/1907.

from the tan bark under the conditions of operation. Fernekes[1] describes a special combustion furnace for the fractional oxidation of methane, whilst Otto[2] suggests the use of ozone as an oxidant. Lacy[3] describes the direct chemical conversion process, $CH_4 \rightarrow CH_3Cl \rightarrow CH_3{\cdot}OH$, whilst Lance and Elsworthy[4] claim the production of methylamine by hydrogenation of hydrocyanic acid over a metal catalyst with subsequent decomposition of the amine with steam in the presence of a catalyst :

$$CH_3{\cdot}NH_2 + H_2O \rightarrow CH_3{\cdot}OH + NH_3.$$

Bone and Wheeler showed that a 20 per cent. yield could be obtained by the flameless combustion of methane on borosilicate glass beads.

The fractional oxidation of other alcohols can be accomplished in like manner. Thus, glycerine in the presence of air will give small quantities of glycerine aldehyde in the presence of platinum black, ethyl alcohol and air passed over platinised pumice at a dull red heat yields 16·8 per cent. of acetaldehyde, eugenol in a similar manner yields 2·9 per cent. of vanillin. It will, however, be noted that the yield of aldehyde is invariably small when the process of fractional combustion is adopted, whilst the catalytic dehydrogenation processes, on the other hand, usually give good yields with very small losses.

THE FRACTIONAL OXIDATION OF HYDROCARBONS

A few experiments have been made on the fractional combustion of hydrocarbons. We have already referred to the attempts to utilise methane as a source of alcohol and formaldehyde. Sabatier and Mailhe[5] have shown that small quantities of aldehydes and alcohols can be produced by the catalytic combustion of the other paraffinoid hydrocarbons,

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[1] U.S.P. 1038546/1912.

[2] *Ann. Chim. Phys.*, 1898, (vii), **13**, 77.

[3] B.P. 16194/1914.

[4] B.P. 4409/1906.

[5] *Compt. rend.*, 1906, **142**, 1394.

using copper, nickel, and cobalt oxides as well as those of chromium, manganese, and uranium at 200°.

Woog[1] has successfully converted benzene into benzoic acid, using coke at 200° as a catalytic agent. Toluene gave a yield of 20 per cent. of benzylaldehyde at 280° on ferric oxide, whilst on nickel oxide at 150° or copper oxide at 220° small quantities of benzaldehyde were obtained.

THE PREPARATION OF ACIDS

The further oxidation of the aldehydes into the corresponding acids by a catalytic process has been successfully developed in the case of acetaldehyde ; as catalyst, manganese acetate, or more rarely the formate, butyrate, lactate, or benzoate, dissolved in acetic acid is employed in the proportion of 300 kilos. of aldehyde to three kilos. of manganese acetate. Aeration is accomplished under pressure, and the aldehyde is converted practically quantitatively into acetic acid. Several difficulties were associated with the earlier phases of the process. The reaction is strongly exothermic, and a very efficient cooling system has to be employed ; at the same time a sufficient depth of liquid to ensure proper aeration must be maintained. All metals sufficiently robust to stand the pressures employed are rapidly attacked under the combined influence of oxygen and acetic acid, thus entailing a heavy repair bill. Pure aluminium liners are frequently employed. The most serious difficulty is the danger of explosion associated with the formation of the extremely unstable peracetic acid, $CH_3 \cdot CO \cdot OOH$, under continued aeration in the presence of the manganese salt ; over aeration has thus to be carefully avoided. Grünstein and Behrens have shown that other catalytic substances such as the oxides of vanadium, uranium, cerium, and iron possess an activity equal to that of the manganese salts,[2] but that their use is attended with a greater risk of explosion, since these salts are not specially active in the removal of

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[1] *Compt. rend.*, 1907, **145**, 124.

[2] B.P., 17424/1911.

the peracetic acid by reduction with aldehyde according to the equation

$$CH_3{\cdot}CO{\cdot}OOH + CH_3{\cdot}CHO = 2CH_3{\cdot}COOH,$$

a reaction which is accelerated by manganese. In technical working a 30 per cent. loss occurs, due to further oxidation of the acetic acid to carbon dioxide and water.

Ethyl alcohol can be directly oxidised to acetic acid by admixture in the vapour state with air and passage over platinum black or vanadium pentoxide.

The preparation of oxalic acid by the oxidation of sugar and starches is no longer accomplished by means of hot nitric acid, which entails a very considerable loss in the form of carbonic, tartaric, mucic, and saccharic acids, but use is made of the observation[1] of Naumann, Moeser, and Lindenbaum that the addition of 0·2 per cent. of vanadic oxide effects the conversion almost quantitatively in the cold in from ten to twenty hours.

THE USE OF CATALYTIC OXIDATION PROCESSES IN THE DYE INDUSTRY

Aniline black.—The preparation of aniline black, one of the most important dyes for cotton yarns, was first developed by John Lightfoot, of Accrington, in 1863, and is now largely employed in all the dyeing industries.

The constitution of the dye was proved by A. G. Green,[2] who contributed a very important addition to the number of catalytic oxidation processes of technical importance. Aniline black is essentially an oxidation product of aniline; during its course of oxidation, three distinct stages of oxidation can be observed.

(1) Emeraldine, which is blue in the form of the free base and gives green salts.
(2) Nigraniline, which is a dark blue base and gives blue salts.
(3) Ungreenable black or aniline black.

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[1] *J. pr. Chem.*, (ii), 1907, **75**, 146.

[2] *J. Chem. Soc.*, 1913, **103**, 932.

According to Green, oxidation proceeds by a series of quinonoid additions in the following order :

$$C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}NH_2$$

$$\downarrow$$

$$C_6H_5{\cdot}N{:}C_6H_4{:}NH$$

(Caro's yellow imide.)

$$\downarrow \ \text{Direct quinonoid addition (acid conditions)}$$

$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}C_6H_4{\cdot}NH$$

(Willstätter's blue imide)

$$\downarrow \ \text{Oxidation}$$

$$C_6H_5{\cdot}N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NH$$

(Willstätter's red imide)

$$\downarrow$$

$$C_6H_5{\cdot}N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}N{\cdot}[C_6H_4{\cdot}NH]_3{\cdot}C_6H_4{\cdot}NH_2$$

Emeraldine

$$\downarrow \ \text{Oxidation}$$

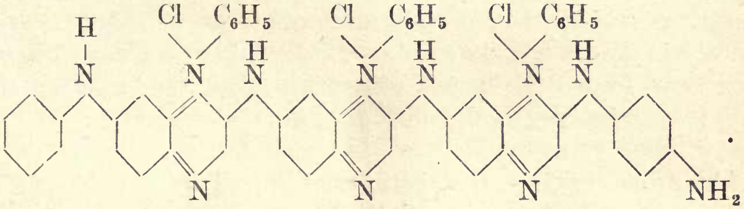
$$C_6H_5{\cdot}N{:}C_6H_4{:}N{\cdot}[C_6H_4{\cdot}N{:}C_6H_4{:}N]_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$$

$$\downarrow O_2$$

$$C_6H_5{\cdot}N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$$

Nigraniline

$$+C_6H_5{\cdot}NH_2{\cdot}HCl$$



Aniline black.

The usual oxidising agents employed are bichromates or sodium chlorate, whilst copper sulphate, copper sulphide (prepared by the double decomposition of copper sulphate and sodium sulphide), or vanadium chloride are used as catalysts.

For example : a 15 per cent. aniline hydrochloride solution (neutralised with free base), with 5 per cent. of sodium chlorate as oxidising agent, is mixed with 5 per cent. of a 54 per cent.

copper sulphide paste to form an effective dyeing-bath. The quantity of vanadium salt required to exert the same catalytic activity as the copper salts normally employed is far less. Sabatier[1] states that only 1 part in 70,000 parts of aniline is required; Witz estimates the ratio at 1 : 270,000, whilst the following is the composition of a dye-bath actually employed.

Parts by weight:

8 per cent. aniline hydrochloride.
1·5 per cent. aniline.
4 per cent. sodium chlorate.
5 per cent. vanadium salt solution.

The solution of the catalytic material is made as follows: 8 grams of ammonium vanadate are dissolved in 40 grams of 30 per cent. hydrochloric acid and 80 c.c. of water. Ten grams of glycerin are added, and the whole is made up to 2 litres. The ratio aniline salt to vanadium salt is approximately 47,500 : 1. This dyeing-bath is, it is stated, not so good as the copper sulphide catalyst bath, since it is rather too rapid in operation, and part of the dye is deposited in the solution itself or loosely adherent to the fibre.

Green[2] in 1907 made the interesting discovery that bichromate and chlorates could be replaced by air as oxidising agent provided that certain promoters were added to the catalytic agents usually employed. In this way a considerable economy in materials was effected and all tendering of the fibre occasioning weakening due to the formation of the oxycelluloses was avoided.

As promoters, small quantities of a *p*-diamine or *p*-amidophenol were found most effective. The use of amidophenol, *p*-phenylenediamine and its sulphonic and carboxylic derivatives, dimethyl-*p*-phenylenediamine, *p*-amidophenylaniline, benzidine, diamidodiphenylaniline, quinone, mono- and di-imides and their chlorides, *p*-nitrophenol, nitrodimethylaniline, *p*-amidophenylquinonimide and their homologues and derivatives, is claimed.

The addition of 4 per cent. of the promoter on the weight of aniline taken is said to be sufficient. The mechanism of

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[1] "La Catalyse."

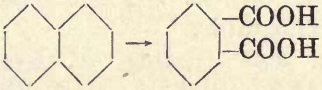
[2] B.P. No. 16189/1907.

operation has not been fully explained, but the catalyst probably hastens the oxidation process by the intermediate formation of complex indamines. Iron, cerium, uranium, and osmic salts exert similar catalytic activity in this oxidation process, but have not received technical application.

Methyl violet and fuchsine.—Cupric chloride and small quantities of phenol are frequently added in the oxidation of dimethylaniline to methyl-violet. It is said that with suitable proportions of catalyst and promoter (phenol) the oxidation can be effected with atmospheric oxygen in lieu of the sodium chlorate usually employed.

In the oxidation of aniline and *o*- and *p*-toluidine to fuchsine, nitrobenzene can be used as oxidising agent in the presence of a small quantity of a vanadium salt or slightly larger quantities of ferric chloride.

Indigo.—Heumann's synthesis of indigo, which was successfully developed by the Badische Co., was based upon the primary conversion of crude naphthalene into phthalic acid, utilising fuming sulphuric acid as an oxidant.



It may be noted in passing that the growth of the contact sulphuric acid process in Germany was determined by the demand for fuming sulphuric acid in the production of this dye.

Groebe[1] accidentally discovered that mercury was an effective catalytic agent in this process of oxidation between 200° and 300°. Further investigation, singularly enough, proved that mercuric sulphate was one of the most effective; copper sulphate, although exerting a reasonable catalytic activity, is inferior, although a mixture of copper and mercuric sulphates is superior to either constituent used singly.[2] Nickel and iron are slightly active, whilst the salts of manganese, potassium, and magnesium are inactive.

The use of a small globule of mercury or a strip of copper in the usual Kjeldahl process of nitrogen estimation is a

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[1] *Ber.*, 1896, **29**, 2806.

[2] Bredig and Brown, *Zeitsch. physikal. Chem.*, 1903, **46**, 502.

striking application of these catalysts to the oxidation of nitrogenous organic matter by strong sulphuric acid.

The patents of Rosenthal[1] also illustrate the oxidising action of mercury salts. The 10 per cent. yield of tertiary bases of the aromatic group obtained by oxidation of tertiary aromatic amines with sulphuric acid at temperatures above 200°, is increased to a 60 per cent. yield in presence of mercury.

AUTO AND INDUCED OXIDATION

The term autoxidation is generally given to those processes of combustion in oxygen or air which take place at the ordinary temperature and proceed with a slow but measurable velocity under these conditions.

Well-known cases are found in the combustion of phosphorus, in the oxidation of certain organic compounds such as benzaldehyde, turpentine, and ether, linseed and similar "drying" oils, in the conversion of sulphites of sodium and zinc into sulphates, and in the corrosion or rusting of many metals, the important cases of zinc and iron being already subjects of an extensive bibliography.[2]

The corrosion and rusting of iron.—Many theories have been advanced to explain the mechanism of iron corrosion when exposed to air and moisture, amongst the more important being the so-called "acid" theory and the electrolytic theory. On the former basis, corrosion is determined by the condition of the moisture in contact with the metal; pure water, or even water containing electrolytes which do not disturb the equality of the concentrations of hydrogen and hydroxyl ion, should completely inhibit all corrosion; small traces of any acid, however, usually carbonic acid derived from the air, should bring about oxidation of the iron, according to the reactions:

$$Fe+H_2CO_3=FeCO_3+H_2$$
$$FeCO_3+H_2O=Fe(OH)_2+H_2CO_3.$$

The actual evolution of hydrogen is, however, not observed

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[1] D.R.P. 127179 and 127180.

[2] See especially "The Corrosion and Preservation of Iron and Steel," A. S. Cushman and H. A. Gardner, 1910.

under these conditions, and so it is further assumed that such hydrogen is oxidised by the dissolved oxygen in the water.

$$2H_2+O_2=2H_2O$$

The *experimentum crucis* of this theory, namely, the incorrodibility of iron in pure water and carbon dioxide-free air has given uncertain results, but it is now generally accepted that corrosion will take place under these conditions, negative results in the experiments being attributed to the retarding influence of small quantities of alkali derived from the glass vessels.

On the other hand, the electrolytic theory has received ample support from the experiments of Whitney, Cushman, and Whipple in America, and by Tilden, Walker, and Lambert in England. According to the electrolytic view, the cause of corrosion is not so much the nature of the electrolyte in contact with the metal but the condition of homogeneity on the metal surface.

It is assumed that in ordinary iron there exists in the form of impurities a certain number of nuclei possessing, in the surrounding solvent, an electrolytic solution pressure inferior to that of the iron itself. In this way a number of small electrolytic cells are set in operation over the surface of the metal. Under ordinary conditions these cells rapidly become polarised, and a molecular film of hydrogen is formed on the cathodic nuclei.

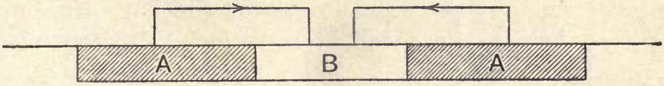

Fig. 14.

Although the electrolytic solution pressures of iron and zinc are, theoretically, sufficiently great to liberate hydrogen from water, yet, owing to the large quantity of energy required actually to form a small bubble of gas in a liquid having a high surface tension such as water, equilibrium is arrived at before a rupture of the metal liquid skin occurs.

The rate of corrosion is then governed entirely by the conditions necessary for the removal of hydrogen. Part of the gas is doubtless removed by solution in the water, and part by combination with atmospheric oxygen, and thus, in small volumes of water, it is the presence of oxygen and not acids which determines corrosion.

It may be noted in passing that on this hypothesis the conditions necessary for corrosion are capable of more precise statement than those on the acid theory. On the other hand, more than one limiting condition must be postulated. These may be enumerated.

(1) The water in contact with the iron must be conducting. Although it may be assumed that pure water is sufficiently good a conductor not entirely to inhibit corrosion, yet the presence of any electrolyte must exert a catalytic effect on the rate of corrosion, provided that the added electrolyte does not alter or modify any reaction taking place at the electrodes.

(2) Homogeneous iron will not corrode. The presence of nuclei of different electrolytic solution pressure from the iron must necessarily be present before corrosion can take place.

Although we assume that in pure electrolytic iron the alteration in electrolytic solution pressure of parts of the metal by local compression or strain, by a difference in crystal size of the metal grains, by the presence of allotropes, or even by an exposure of the cube face (1, 0, 0) in juxtaposition to another crystal face, *e.g.*, of the octahedron (1, 1, 1), may all contribute to a slow corrosion occurring in the purest metals, yet, here again, specific impurities of different electrolytic solution pressures must exert a very marked catalytic action.

For example, in steel corrosion or "pitting" it has been found by G. and M. Whipple that mill scale, magnetic oxide of iron (Fe_3O_4), is extremely active as a corrosion catalyst, being more important than ordinary red rust itself (Fe_2O_3). Doubtless, this great activity is due, not only to its function as a corrosive cell electrode, but also to its action as a catalyst in the combination of the dissolved oxygen and cathode hydrogen, which reaction velocity, as we have seen, governs the actual rate of corrosion.

Cushman[1] investigated the influence of the pigments usually

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[1] *Loc. cit.*

employed for the protection of iron-work on the rate of corrosion of iron; we may conveniently classify them under the groups (1) catalytically active, (2) inactive, (3) catalytically negative.

(1)

Lamp black.
Precipitated barium sulphate
Ochre.
Bright red oxide.
Carbon black.
Graphite.
Barium sulphate.
China blue.

(2)

White lead—basic carbonate.
Sublimed lead—basic sulphate
Sublimed white lead.
Lithopone.
Orange mineral.
Red lead.
Litharge.
Venetian lead.
Calcium carbonate.
China clay.

(3)

Zinc and lead chromate.
Zinc oxide.
Zinc chromate.
Zinc and barium chromate.
Zinc and lead white.
Prussian blue.
Chrome green.
Ultramarine blue.
Willow charcoal.

It is interesting to note that all the chromates come within the third category, doubtless owing to the passifying action of these salts.

From the work of Burgess, Austin, Friend, Cushman, and others the following preliminary classification of the catalytic influence of the elements on the corrosion of iron may be given.

Catalytically active.	Inert.	Slightly negatively catalytic.	Negatively catalytic.
Selenium.	Aluminium	Lead.	Copper.
Sulphur.	Arsenic.	Cobalt.	Nickel.
(Silicon).	Silver.	Tin.	Chromium.
Phosphorus.	Tungsten.	Manganese.	Silicon.
Carbon up to 0·82 per cent.			

It must, however, be admitted that the above classification should be regarded as purely provisional, since the tests have usually been accomplished on cast or wrought iron or on the simpler steels, in which case the physical and chemical changes caused by the addition of small quantities of carbon to pure iron and the varied natures of the components of the iron–carbon system, when subjected to different thermal treatment, as well as the unavoidable presence of traces of the more common impurities, especially phosphorus, silicon, sulphur, and manganese, are sufficient to make comparisons lacking in scientific accuracy. It may, however, be pointed out that in the case of binary alloys the components of which form a continuous series of solid solutions, the corrosion cells will be very small, of atomic or molecular dimensions, and thus, corrosion will be perfectly uniform and free from pitting. If the components form conglomerates either in the process of manufacture or due to segregation in the solid state (*e.g.*, manganese sulphide in certain steels), the potential distribution on the surface will be non-uniform in character, and rapid corrosion accompanied by pitting may be expected. Similar results may be obtained with immiscible solid solutions.

INDUCED OXIDATION

We have already noted that the conditions under which metals may undergo autoxidation are extremely varied, but that the evidence points to the correctness of the electrolytic theory, the mechanism of corrosion catalysts being easily interpreted from this point of view. It has, however, been tacitly assumed that the oxygen functions solely as a simple depolarising agent for the small electrolytic cells formed on the surface of the metals. It is evident, however, that, in this simple form, the theory cannot be extended to non-conductors, nor does it throw any light on the mechanism of those interesting cases of induced oxidation first investigated by C. F. Schönbein[1] which accompany the autoxidation of many substances.

Schönbein showed that during many processes of autoxidation for every molecule of oxygen consumed by the substance undergoing oxidation, a molecule of oxygen was simultaneously transformed into a more active state; this active oxygen could then secondarily react either with more oxygen to form ozone, with water to form hydrogen peroxide, or, in the presence of other oxidisable substances, could oxidise them, frequently causing oxidations which cannot be accomplished by ordinary

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[1] *J. pr. Chem.*, 1858 to 1868, 73 to 99.

atmospheric oxygen. For example, hydrogen peroxide is formed during the rusting of lead, zinc, and probably iron; ozone is formed during the oxidation of phosphorus. Indigo is converted into isatin during the autoxidation of palladium hydride, benzaldehyde, or turpentine. Various of the more important theories which have been advanced to explain the mechanism of these processes may be briefly classified as follows :—

The dualistic theory.—Schönbein[1] was of the opinion that these cases of autoxidation were best interpreted on C. Brodie's[2] hypothesis, in which ordinary oxygen during the process of oxidation is split up into two parts, "ozone" and "antozone."

$$O_2 \begin{array}{l} \nearrow \overset{-}{O}, \text{ or ozone.} \\ \searrow \overset{+}{O}, \text{ or antozone.} \end{array}$$

R. Clausius[3] more definitely stated that Brodie's ozone and antozone could be regarded as atomic oxygen of opposite electric charges

$$O_2 \rightarrow \dot{O} + O'.$$

van't Hoff,[4] as a result of his experiments on the autoxidation of phosphorus, introduced the hypothesis that atmospheric oxygen is, already prior to any process of oxidation, normally partly dissociated into charged atomic oxygen and that the equilibrium $O_2 \rightleftarrows \dot{O} + O'$ must be considered as an important factor in oxidation phenomena.

According to the above hypothesis, all processes of autoxidation are dual in character, two substances simultaneously undergoing oxidation. Engler[5] has attempted to distinguish between these, by terming the substance undergoing oxidation the autoxidiser, and the substance simultaneously oxidised the acceptor. It is evident that either the autoxidiser or the acceptor may react, on the one hand, with the ozonic, or, on the other, with the antozonic form of the active oxygen,

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[1] *Loc. cit.*

[2] *Phil. Trans.*, 1850, **141**, 759 *et seq.*

[3] *Pogg. Ann.*, 1858, **103**, 644.

[4] *Zeitsch. physikal. Chem.*, 1895, **16**, 411.

[5] "Kritische Studien über die Autoxydationsvorgänge, Braunschweig," 1903.

depending on the chemical nature of the substances undergoing oxidation; thus, water, phosphorus, the alkali metals, and the alkaline-earth metals form antozonides on oxidation, whilst ozone and the chromates, permanganates, hypochlorites, and vanadates, as well as lead, zinc, nickel, bismuth, silver, and manganese oxides, are ozonides.

Van't Hoff noticed that in the case of phosphorus undergoing atmospheric oxidation in the presence of indigo acting as acceptor, a continuous supply of fresh acceptor was required to maintain the velocity of oxidation up to a measurable speed. He consequently argued that the reaction $O_2 \rightleftarrows \dot{O} + O'$ must be a reversible one, since the accumulation of the ozonic form of active oxygen normally removed in the oxidation of the indigo to isatin retarded the action of the antozonic oxygen on the phosphorus.[1]

It must be admitted that a search for the charged ozonic modification of oxygen which should be present in the air after passage over phosphorus has yielded conflicting results. Elster and Geitel[2] noted that air thus treated was electrically conducting,[3] and Goekel[4] showed that this conductivity was not due to the presence of ozone, which could be absorbed without destroying the conductivity. Barus,[5] Harms,[6] and Bloch,[7] on the other hand, have shown that the conductivity cannot be attributed to the ozonic oxygen or charged ionic oxygen, but is due to oxides of phosphorus collected round charged nuclei forming aggregates of relatively large dimensions ($r = 10^{-6}$ cm.), whilst the actual number of charged ions observed fell far short of the stoichiometric ratio, oxygen absorbed : oxygen ionised $= 1 : 1$, postulated by the hypothesis.

E. Hoppe-Seyler[8] and Baumann adopted the same hypothesis as Schönbein, but substituted the term "nascent"

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[1] See J. Joubert: "Thèse sur la Phosphorescence du Phosphore," 1874; T. Ewan [*Phil. Mag.*, 1894, (v), **38**, 512]; J. Chappuis [*Bull. Soc. chim.*, 1881, (ii), **35**, 419].

[2] *Wied. Ann.*, 1890, **39**, 321; *Physikal. Zeitsch.*, 1903, **4**, 457.

[3] See also Mattenci ("Encyc. Brit.," 1855, **8**, 622); Naccari (*Atti della Scienze de Torino*, 1890, **25**, 252).

[4] *Physikal. Zeitsch.*, 1903, **4**, 16.

[5] "Experiments with Ionised Air," Washington, 1901.

[6] *Physikal. Zeitsch.*, 1902, **3**, 111.

[7] *Ann. Chim. Phys.* 1905, (viii), **4**, 25.

[8] *Zeitsch. physiol. Chem.*, 1878, **2**, 22.

oxygen for Schönbein's ozonides and antozonides; according to these investigators, processes of autoxidation may be represented by the general equation

$$X + O_2 \rightarrow XO + \text{nascent oxygen},$$

and such nascent oxygen was to be regarded as possessing superior activity to the substance in the ordinary molecular state. It is evident that the difference in view is one of nomenclature rather than of principle.

The intermediate compound theory.—M. Traube,[1] Gisammetti,[2] A. Bach,[3] C. Engler and V. Wild[4] and others developed the hypothesis of the intermediate compound.

Thus, according to M. Traube, the process of autoxidation of the metals with the simultaneous formation of hydrogen peroxide takes place through the presence of water as intermediary, as represented by the equation

$$\boxed{M + O}H_2 + O_2 \rightarrow MO + H_2O_2.$$

Hydrogen peroxide is thus reduced oxygen and not oxidised water as postulated by Schönbein and his co-workers. The curious reducing actions of hydrogen peroxide, *e.g.*,

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

are cited to support this claim.

According to Traube, the stoichiometric ratio,

$$MO : H_2O_2 :: 1 : 1$$

need not necessarily be observed in practice, as the secondary reaction

$$M + H_2O_2 = M(OH)_2$$

may take place. On the electrical theory such a reaction is extremely unlikely, and the usual discrepancy between the theoretical quantity of peroxide and that actually obtained must be put down to thermal decomposition.

The necessity for the presence of at least small quantities of water vapour in processes of combustion[5] has been observed

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[1] *Ber.*, 1882, **15**, 663; 1893, **26**, 1471.

[2] *Abhandlungen*, Berlin, 1899.

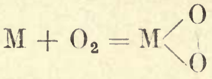
[3] *Compt. rend.*, 1897, **126**, 2, 951.

[4] *Ber.*, 1897, **30**, 1669.

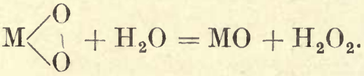
[5] See Mrs. Fulhame, "An Essay on Combustion," London, 1794; H. B. Dixon (*Phil. Trans.*, 1884, **175**, 630; *J. Chem. Soc.*, 1886, **49**, 95), and H. E. Armstrong, (*Brit. Assoc. Reports Proc. Roy. Soc.*), 1886, **40**, 287.

by many independent investigators and its function as an intermediary catalyst or electrolyte to complete the voltaic circuit need not be discussed at this point. The application of this principle to explain certain cases of autoxidation and induced oxidation forms an important extension of the hypothesis. It will be noted that the formation of substances such as ozone, permanganate, and the oxides of the heavy metals, *i.e.*, Schönbein's ozonides, must be considered as secondary reactions taking place between the hydrogen peroxide and the acceptor. In some cases, as, for example, in the formation of ozone from oxygen and hydrogen peroxide, or of silver oxide from hydrogen peroxide and silver, this assumes exceedingly improbable reactions.

A. Bach adopted another point of view, in which an intermediary peroxide was first formed, prior to the decomposition into an oxide and with simultaneous oxidation of the acceptor. Thus, in the oxidation of a metal in the presence of water, a metallic oxide and hydrogen peroxide are assumed to be formed according to the following scheme :



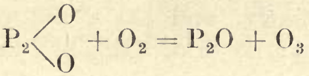
$$M + O_2 = M\Big\langle\begin{matrix}O\\ |\\ O\end{matrix}$$



$$M\Big\langle\begin{matrix}O\\ |\\ O\end{matrix} + H_2O = MO + H_2O_2.$$

In the oxidation of phosphorus with the simultaneous production of ozone we may adopt the equations of Engler and Wild,[1] or of Ostwald[2] to explain the mechanism on Bach's intermediate peroxide theory.

$$(a)\ 2P + O_2 = P_2O_2$$



$$P_2\Big\langle\begin{matrix}O\\ \\ O\end{matrix} + O_2 = P_2O + O_3$$

$$(b)\ 2P + 2O_2 = P_2O_4 = P_2O + O_3$$

giving the stoichiometric ratio $P : O_2 : : 2 : 1$, the ratio actually obtained by van't Hoff.

Bodländer,[3] and Baeyer and Villiger,[4] in researches on the

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[1] *Ber.*, 1897, **30**, 1669.

[2] *Zeitsch. physikal. Chem.*, 1900, **34**, 250.

[3] *Ahrens Sammlung*, 1889, **3**, 470.

[4] *Ber.*, 1900, **33**, 585, 3480.

oxidation of benzaldehyde with indigo as an acceptor, gave additional support to Bach's theory by the isolation of an intermediary peroxide, benzoyl hydrogen peroxide :

$$C_6H_5 \cdot CHO + O_2 = C_6H_5 \cdot CO:O(OH)$$

which peroxide could then react in two distinct ways :

(*a*) With another molecule of benzaldehyde,

$$C_6H_5 \cdot CO:O(OH) + C_6H_5 \cdot CHO \rightarrow 2C_6H_5 \cdot COOH.$$

(*b*) With the acceptor indigo,

$$C_6H_5 \cdot CO:O(OH) + \text{indigo} \rightarrow C_6H_5 \cdot COOH + \text{isatin}.$$

Bach's intermediate compound theory has been extended to other oxidising substances in addition to atmospheric oxygen, for example, to H_2O_2 by Kastle and Lövenhart,[1] H. Fenton[2] and others.

(3) **The energetics theory.**—We have noted that van't Hoff's postulate of partial dissociation of atmospheric oxygen into active ionic oxygen cannot be substantiated by experiment, and that, on Traube's peroxide theory, we cannot easily account for the formation of the "ozonides" of Schönbein. Consequently, we must assume on the above alternative hypotheses of Schönbein and Bach that the active oxygen—either "antozone" or "ozone" or "nascent oxygen" respectively—left over from the oxidation of the autoxidiser, is endowed with more chemical energy than normal atmospheric oxygen. Otherwise, it must be assumed that peroxides formed by the direct union of atmospheric oxygen and, say, a metal are similarly endowed.

The question may at once be raised as pointed out long ago by G. Liveing,[3] "Whence does this increased chemical activity or elevation of the chemical potential of the residual oxygen come ?" It is certainly possible to attribute to most peroxides oxidising potentials or activities greater than atmospheric oxygen, but under these conditions one is at a loss to explain their formation from a metal in the presence

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[1] *Amer. Chem. J.*, 1903, **29**, 397, 517.

[2] *J. Chem. Soc.*, 1899, **75**, 1.

[3] "Chemical Equilibrium the Result of the Dissipation of Energy," Cambridge, 1885.

of air. Further, W. Ostwald[1] showed that the energy degraded during the oxidation of phosphorus cannot be utilised for the production of ozone, assuming that the chemical energy of one system is not available for another totally different reaction. Thus, on the dualistic theory of nascent or active oxygen, the extra energy necessary for the production of the measured activity or elevation of the potential is not forthcoming.

We may, however, adopt the view that Ostwald's assumption, namely, that the chemical energy of one system is not available for another totally different system, is, in these cases of induced oxidation, at least, not correct. It is possible to assume that the energy usually liberated in the form of heat during the oxidation of a metal,

$$2\mathrm{M} + \mathrm{O}_2 \rightarrow 2\mathrm{MO} + \mathrm{Q},$$

may in certain circumstances not be entirely lost to the chemical system as chemical energy and merely be radiated in the form of heat throughout the system, but may be stored as chemical energy in another molecule or number of molecules in the system.

In view of the frequent occurrence of the ratio autoxidator : acceptor oxidised : : 1 : 1, we may further simplify our argument by postulating a simple transfer of energy.

$$\begin{aligned} 2\mathrm{M}+2\mathrm{O}_2&=2\mathrm{MO}+\mathrm{O}_2+Q \\ Q+\mathrm{O}_2+2\mathrm{H}_2\mathrm{O}&=2\mathrm{H}_2\mathrm{O}_2+q' \end{aligned}$$

where Q and $Q-q'$ are the respective heats of reaction. We thus overcome the difficulty of accounting for the energy necessary for the dissociation of oxygen into its atoms or for the production of a very active peroxide.

It may, however, be pointed out that the intermediate peroxide theory of Bach is not entirely excluded on this assumption. In those cases where the direct formation of the peroxide is, *per se*, an exothermic reaction, the oxidising power of the peroxide formed will be less than that of atmospheric oxygen; secondly, we may include those cases where we obtain a fractional formation of a peroxide, in which the oxidising activity or potential is very great and is brought

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[1] *Zeitsch. physikal. Chem.*, 1900, **34**, 248.

about by the transfer of chemical energy from the ordinary process of oxidation to the reactions :

$$M + O_2 = MO_2 \text{ or } 2MO + O_2 = 2MO_2.$$

THE DRYING OF OILS

The use of siccatives to accelerate the drying of the oil in paints and varnishes is a very usual one, and has been the subject of much experimental investigation. It has long been known that linseed oil, when exposed in thin films to the air, undergoes slow oxidation, a property used both in the paint and varnish industry as well as in the manufacture of linoleum.

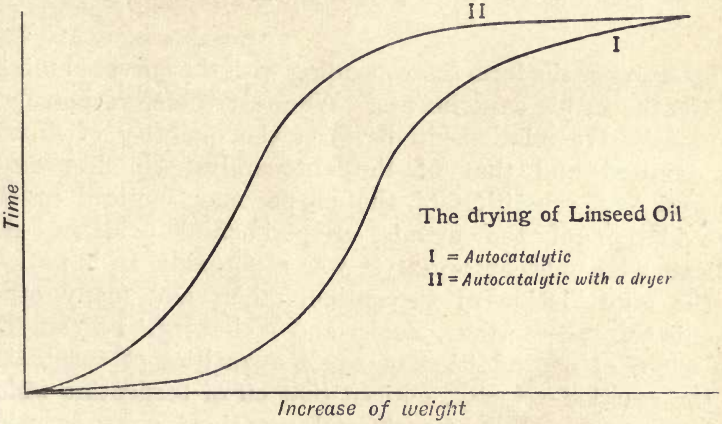

FIG. 15.

Lippert,[1] Weger,[2] and Kissling[3] showed that the "drying" was virtually a process of autoxidation and that linseed oil could absorb or combine with more than 20 per cent. of its weight of oxygen.

The reaction velocity of this processof autoxidation was first examined by A. Genthe,[4] who found that the increase

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[1] *Zeitsch. angew. Chem.*, 1898, **11**, 412.

[2] *Chem. Rev. Fett-Harz-Ind.*, 1899, **4**, 301.

[3] *Zeitsch. angew. Chem.*, 1891, **4**, 395.

[4] *Ibid.*, 1906, **19**, 2087.

of weight time-curve exhibited the usual sinuous character of an autocatalytic reaction (Fig. 15).

It had, therefore, to be assumed that in the oxidation of linseed oil to linoxyn, a product, either an intermediary or the result of some side reaction, was formed, which exerted a catalytic function on the autoxidation of the oil.

If a, b, be the initial concentrations of linseed oil and autocatalyst respectively, then, the rate of oxidation of the oil after a time t when x of the linseed oil has already been oxidised is given by the equation :

$$\frac{dx}{dt} = K(a - x)(b + x),$$

an equation of the form corresponding with the curves obtained by Genthe in his experiments. We must therefore postulate a quantitative relationship between the quantity of linseed oil oxidised and that of the autocatalyst simultaneously generated, a repetition of the phenomenon noticed in the autoxidation of the metals. Experimental evidence also indicated that the autocatalyst was a peroxide, as is noticed in the autoxidation of turpentine, ether, and many other organic substances ; thus, Engler and Weiszberg,[1] who studied the effect of the addition of small quantities of turpentine on the reaction velocity, noticed that oil of turpentine which had been exposed to the air and contained more peroxide than fresh material exerted a superior catalytic activity. Benzoyl peroxide and ether, which have been well shaken with air, likewise accelerated the reaction velocity. In common with other autocatalytic processes which can be attributed to the formation of an unstable peroxide, light exerts a marked catalytic activity. The oxidation also appears to proceed further under intense illumination than in the dark. Genthe[2] found an increase of upwards of 34 per cent. in weight during the oxidation of linseed oil when exposed to ultra-violet light.

Linseed oil which has been boiled does not readily oxidise on exposure to the air, since the autocatalytic material originally present in the oil is destroyed by heat. It resumes its activity, however, on blowing with air.

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[1] *Chem. Zeit.*, 1903, 27, 1196.

[2] *Loc. cit.*

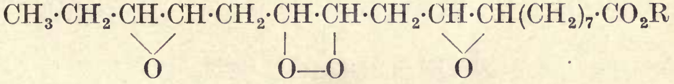
Although the mechanism of the process of drying is fairly clear from the above considerations, the actual chemical changes involved have by no means been elucidated. Hazura,[1] Kissling,[2] Friend,[3] Baly,[4] Gardner,[5] King,[6] Salway[7] and others have shown that several volatile products are evolved during the oxidation of the oil, including carbon dioxide and water vapour and certain toxic substances, notably carbon monoxide and poisonous unsaturated aldehydes such as acrolein. Linseed oil contains the glycerides as well as some of the free acid of a variety of organic acids, including linolenic, linoleic, and oleic acids, as well as smaller quantities of mixed glycerides of stearic, palmitic, and other acids. G. Schicht[8] and Erdmann[9] considered linolenic acid to have the following structure:

$$CH_3\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH(CH_2)_7\cdot CO_2H,$$

and linoleic acid,

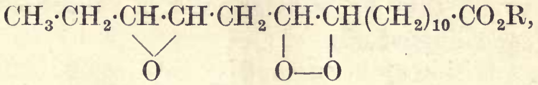
$$CH_3\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH(CH_2)_{10}\cdot CO_2H,$$

the glycerides of which, according to Orloff,[10] undergo oxidation with the formation of peroxides, *e.g.*,



$$CH_3\cdot CH_2\cdot \underset{\diagdown\,O\,\diagup}{CH\cdot CH}\cdot CH_2\cdot \underset{|\quad|\atop O—O}{CH\cdot CH}\cdot CH_2\cdot \underset{\diagdown\,O\,\diagup}{CH\cdot CH}(CH_2)_7\cdot CO_2R$$

and



$$CH_3\cdot CH_2\cdot \underset{\diagdown\,O\,\diagup}{CH\cdot CH}\cdot CH_2\cdot \underset{|\quad|\atop O—O}{CH\cdot CH}(CH_2)_{10}\cdot CO_2R,$$

R being the glycerine radicle.

Fahrion[11] considered that the peroxide present in Orloff's oxidation products would be unstable and undergo intramolecular change to a ketoxy-group, forming, after condensa-

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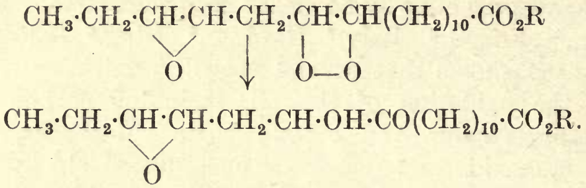
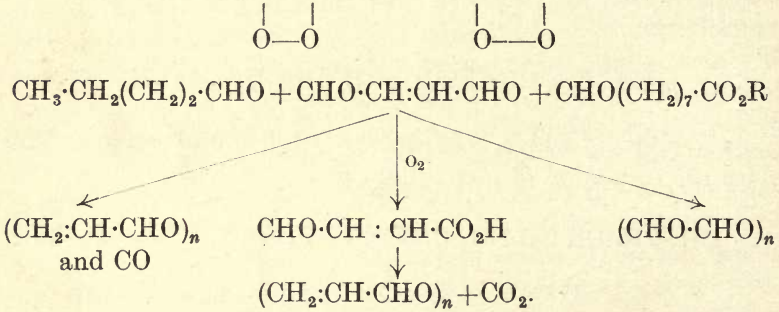
[1] *Zeitsch. angew. Chem.*, 1888, **1**, 312.
[2] *Ibid.*, 1891, **4**, 395.
[3] *Proc. Paint Varnish Soc.*, 1914, 140.
[4] *J. Soc. Chem. Ind.*, 1912, **31**, 515.
[5] *J. Ind. Eng. Chem.*, 1914, **6**, 91.
[6] *Ibid.*, 1915, **7**, 302.
[7] *J. Chem. Soc.*, 1916, **109**, 138.
[8] *Seifenfabrikant*, 1914, **34**, 13.
[9] *Ber.*, 1909, **43**, 1324.
[10] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658.
[11] *Zeitsch. angew. Chem.*, 1910, **23**, 723.

tion and elimination of water, the varnish-like stable solid linoxyn:



$$CH_3\cdot CH_2\cdot\underbrace{CH\cdot CH}_{O}\cdot CH_2\cdot\underbrace{CH\cdot CH}_{O-O}(CH_2)_{10}\cdot CO_2R$$
$$\downarrow$$
$$CH_3\cdot CH_2\cdot\underbrace{CH\cdot CH}_{O}\cdot CH_2\cdot CH\cdot OH\cdot CO(CH_2)_{10}\cdot CO_2R.$$

Salway, on the other hand, whilst postulating a different structure for linolenic acid from Erdmann, accounts for the formation of traces of aldehydes and carbon monoxide and dioxide during the process of autoxidation by postulating the intermediary formation of a dioxygenide.[1]



$$CH_3\cdot CH_2(CH_2)_2\cdot CH=CH\cdot CH=CH\cdot CH=CH(CH_2)_7\cdot CO_2R$$
$$CH_3\cdot CH_2(CH_2)_2\cdot\underbrace{CH\cdot CH}_{O-O}\cdot CH=CH\cdot\underbrace{CH-CH}_{O-O}(CH_2)_7\cdot CO_2R$$
$$CH_3\cdot CH_2(CH_2)_2\cdot CHO+CHO\cdot CH:CH\cdot CHO+CHO(CH_2)_7\cdot CO_2R$$
$$\begin{array}{ccc} \swarrow & \downarrow{\scriptstyle O_2} & \searrow \\ (CH_2:CH\cdot CHO)_n & CHO\cdot CH:CH\cdot CO_2H & (CHO\cdot CHO)_n \\ \text{and } CO & \downarrow & \\ & (CH_2:CH\cdot CHO)_n+CO_2. & \end{array}$$

Linoxyn would thus be, substantially, a condensed aldehyde in unchanged linseed oil.

On the addition of very small quantities of siccatives such as the salts of manganese, lead, zinc, and, more rarely, cobalt, vanadium, and uranium, the drying process is considerably shortened and the **S**-shaped curve follows that indicated by II.[2]

It is still a matter of dispute whether the siccative is a catalyst, *per se*, for the oxidation of linseed oil or, whether it catalytically hastens the formation, or stabilises the presence, of the autocatalytic peroxide and thus exerts a pseudo-catalytic function.

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[1] See Salway and Kipping, *J. Chem. Soc.*, 1909, **95**, 166.

[2] See p. 149, *ante*.

If initially present in very large quantities the quantity of autocatalyst may be neglected and the form of the curve would be represented by the simple equation

$$\frac{dx}{dt}=k'(a-x),$$

Some experiments, however, by E. Rideal, point to the persistence of the "period of induction," followed by a rapid rise in the value of $\frac{dx}{dt}$; we must therefore assume that the siccative is pseudo-catalytic in behaviour and serves either to stabilise or assist in the formation of the autocatalytic peroxide.

The metallic salts of weak acids are usually employed, *e.g.*, the borates. These, however, suffer from the disadvantage of being insoluble in the oil. Under these conditions, the influence of the siccative present as a heterogeneous phase in the oil is not very marked and, at the same time, the small solid particles present in the oil, even when they are chemically inert, as, for example, in the case of silica or barytes, act as negative catalysts,[1] since they assist in the decomposition of the autocatalytic peroxides. For this reason, soluble organic salts, usually the soaps, are generally employed. Lead oleate, cobalt linoleate and manganese rosinate are examples of such soaps.

Ingle,[2] and Mackey and Ingle,[3] as a result of a long series of investigations on the action of siccatives, arrived at the following conclusions:

(1) In its oil soluble form, *i.e.*, as a soluble metallic soap, those metals which exist in more than one state of oxidation act as driers, provided that the salts of the lower oxides are more stable than those of the higher oxides.

(2) Metals which form a number of oxides are more active than the mono- or di-valent metals.

The results obtained in the investigations of Ingle are summarised in the following table (Fig. 16). The black lines indicate the time required for 7 grams of cotton-wool, oiled with 14 grams of linseed oil (iodine value 178), and mixed

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[1] Gardner, *J. Ind. Eng. Chem.*, 1914, **6**, 91.

[2] *J. Soc. Chem. Ind.*, 1916, **35**, 454.

[3] *Ibid.*, 1917, **36**, 317

with 2 per cent. of metallic soap, to attain a temperature of 200° in a cloth oil-tester. The shaded lines give the corresponding times required for 14 grams of olive oil (iodine value 55) to attain the same temperature under similar conditions.

Copper proved to be somewhat erratic in behaviour, acting first as an accelerator and subsequently inhibiting the oxidation. It was shown that this action was due to the precipitation of cuprous oxide in the oil on elevation of the temperature.

It will be noted that both sodium and silver show catalytic activities which are considerably higher than would be expected from Mackey and Ingle's generalisations, and for which no explanation is as yet forthcoming.

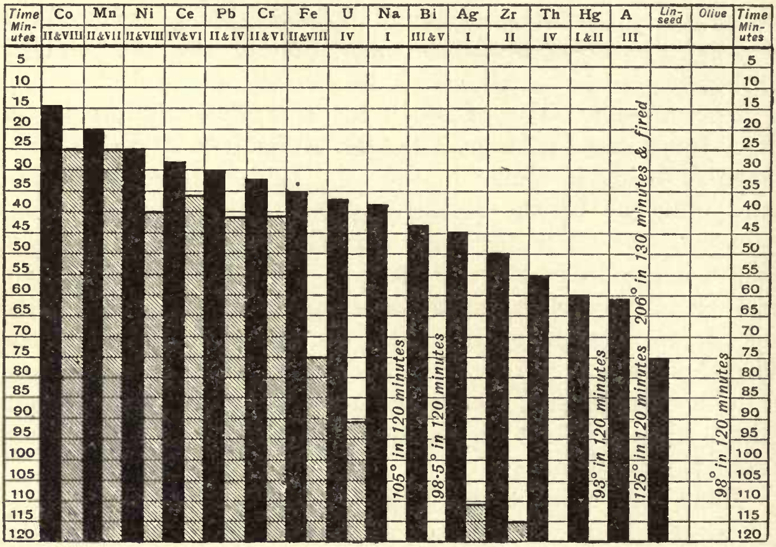


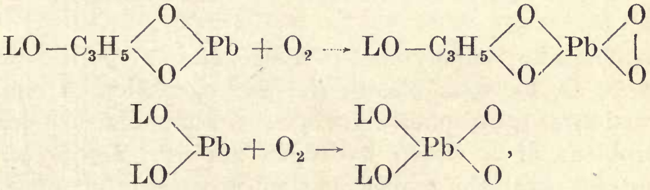
FIG. 16.

Further investigation on the influence of $\dot{H}$ and OH′, on the reaction velocity may indicate that the optimum conditions are to be found when the oil, which always contains small quantities of water resulting from the autoxidation, is slightly alkaline, the sodium soap serving to neutralise the small quantities of relatively strong acids, such as acetic and formic acid, which are by-products of the oxidation. In the case of the silver soap, the precipitation of colloidal silver, especially since Cu_2O has been shown to be formed above 100°, may be expected, and this would probably show enhanced activity as an oxygen carrier.

Ingle attributes the action of siccatives to the intermediary formation of peroxides. Thus, on the addition of litharge to linseed oil, partial saponification of the glyceryl linolenate results in the formation of lead linolenate and glyceryl plumbolinolenate :

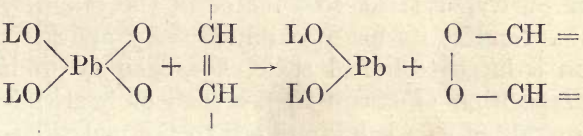
$$C_3H_5(OL)_3 + 2PbO \rightarrow PbO_2{\cdot}C_3H_5OL + Pb(OL)_2.$$

Both these lead salts can form compounds with atmospheric oxygen to give compounds of tetravalent lead.



in which L denotes the linolenic acid radicle.

Further reaction may then occur with the unsaturated double linkages of the fatty acids and glycerides present in the oil,



and thus hasten the normal oxidation velocity of the oil.

CHAPTER V

HYDROGEN AND HYDROGENATION

THE MANUFACTURE OF HYDROGEN

THE increasing employment of hydrogen in modern technical processes, as, for example, in the hydrogenation of oils and the fixation of atmospheric nitrogen as ammonia, has created the problem of a cheap hydrogen supply. Moreover, the demand in catalytic hydrogenation processes for purity of materials necessitates in many cases the production of hydrogen in a high degree of purity.

The sources of hydrogen supply are various. Electrolytic hydrogen, naturally, can be readily obtained with the necessary degree of purity, but the cost factor in the majority of circumstances renders its use prohibitive. By another method, in use on a large technical scale, hydrogen is produced by the decomposition of steam in presence of heated iron, the resulting oxide of iron being reduced to the metallic condition by means of water-gas. With careful regulation, this process may be made to yield hydrogen of the requisite purity. Without due attention, however, the presence of prohibitive concentrations of carbon monoxide in the gas, resulting from the action of steam on carbon deposited in the iron from the water-gas during the reducing phase, may render the hydrogen unsuitable for use in certain catalytic operations. Furthermore, the economy of the process is, at present, low, and the cost factor, therefore, somewhat high.

The analogous process of Bergius, already investigated upon a small technical scale, generates hydrogen under high pressure and with great purity, by the action of liquid water upon finely divided iron at moderate temperatures in closed steel bombs. The pressures employed are generated by the reaction itself and are sufficient to maintain the water in the liquid state. The temperatures required, apart from the initial heat necessary to start the reaction, are maintained by the exothermicity of the reaction. Like the previous method of preparation. the process is discontinuous, the oxide of iron produced simultaneously with the hydrogen requiring subsequent reduction to the metallic state.

Hydrogen may also be produced from water-gas by liquefaction of the carbon monoxide at the temperatures of liquid air boiling under reduced pressures. By this method complete separation of the constituents of the water-gas is not readily attainable and, in common practice, a hydrogen containing from 2 to 3 per cent. of carbon monoxide is generally obtained. A more complete separation of the two gases may only be obtained with a prohibitive decrease in the yield of hydrogen, since a mixture of hydrogen with 2 per cent. of carbon monoxide behaves almost exactly like hydrogen in its physical properties. Actually, the yield of hydrogen would be considerably increased if a 95 per cent. hydrogen were obtained by the liquefaction process, the remaining 5 per cent. of carbon monoxide being subsequently removed by other means.

The water-gas catalytic process.—The most recent technical method for the production of hydrogen, and in many ways the most promising as regards cheapness of production, involves a catalytic operation using water-gas and steam as the reaction materials. In the presence of suitable catalytic agents, at regulated temperatures, carbon monoxide and steam react to yield carbon dioxide and hydrogen. Utilising water-gas, therefore, a gas rich in hydrogen would result, the problem of further purification involving the removal of the carbon dioxide formed and of the unconverted carbon monoxide.

The reaction occurring, which may be formulated by means of the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

is in reality an equilibrium process, the direction of the reaction being governed by the temperatures maintained and the concentrations of the respective components. The equilibria obtaining at various temperatures may, in the absence of experimental data over the whole range of temperatures required, be calculated from the experimental work of De Hahn[1] at higher temperatures. In this way the following approximate values for the equilibrium constant

$$K = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}$$

at the various temperatures are obtained.

T.	400°	500°	600°	700°	800°
K.	0·05	0·1	0·3	0·6	0·9

From these figures it is obvious that high temperatures favour the production of carbon monoxide in agreement with experience in water-gas manufacture. Lower temperatures favour the production of carbon dioxide and hydrogen. The lower the temperature at which the water-gas reaction occurs, the greater will be the conversion of carbon monoxide to dioxide with the corresponding increase in yield and purity of hydrogen. On the other hand, decrease of temperature slows down the reaction velocity, so that, in practice, a low limit to the temperature will be set below which attainment of equilibrium conditions requires the presence of catalytic agents. It is obvious from these facts that, for the successful production of hydrogen from water-gas, catalytic agents are required which will rapidly promote the reaction at as low a temperature as possible.

A considerable patent literature relative to this process already exists. The basic patent for the production of hydrogen from gases containing the same in admixture with carbon monoxide and hydrocarbons was granted to Mond and Langer.[2] According to this invention, the gases were to be passed with excess of steam over heated catalysts, for example, nickel at temperatures of 350–400°, cobalt at 400–450°. The hydrocarbons were said to be decomposed, while the carbon monoxide was converted to the dioxide,

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[1] See Haber, "Thermodynamics of Technical Gas Reactions."

[2] B.P. 12608/1888.

which was thereupon removed. It was subsequently claimed that the gas produced was almost free from carbon monoxide. Elworthy suggested the employment of nickel or iron in a similar manner with a mixture of water-gas and steam. A patent of Pullman and Elworthy[1] proposes to separate the carbon dioxide and hydrogen by processes of diffusion and of fractional solution. In 1907, Vignon applied for a patent[2] for a process as above, using iron or oxides or platinum at red heat. The patent was not granted. Ellis and Eldred[3] employed nickel, iron, or manganese for catalytic agents of the water-gas–steam reaction, using a specially designed superheated reaction chamber. Näher and Müller[4] suggest the use of a contact mass of rhodium or palladium asbestos at a working temperature of 800°. They claim a product with less than 0·4 per cent. of carbon monoxide. It is obvious that at a temperature of 800° such a low content of carbon monoxide can only be obtained by the use of large excesses of steam, which would render the process economically impossible. More recently, a considerable number of patents have been obtained by the Badische Anilin- & Soda-Fabrik relative to the process, which has been established by them on a commercial basis. B.P. 26770/1912 calls for the carrying out of the process under pressures of 4–40 atmospheres at temperatures between the limits of 300° and 600°, using nickel and cobalt as catalysts. The increase in pressure facilitates the reaction velocity and ease of heat regeneration. So conducted, it was claimed to be specially useful for small carbon monoxide content. Later, in 1912,[5] an improvement was patented for the maintenance of the requisite temperature in the catalytic mass by the addition of air or oxygen, which, combining with some of the hydrogen, generated sufficient heat to enable the process to be maintained continuously, especially if only small amounts of carbon monoxide were present. A patent of 1913[6] by the same company deals with suitable catalysts, the basis of which was oxide of iron with suitable binding agents. B.P. 8864, 1913, is concerned with catalysts containing nickel and similar substances, which apparently tend towards the simultaneous production of

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[1] B.P. 22340/1891.
[2] B.P. 20685/1907.
[3] U.S.P. 854157/1907.
[4] B.P. 20486/1911.
[5] B.P. 27117.
[6] B.P. 27955.

methane, since B.P. 27963/1913, deals with catalysts which do not produce methane by side reaction. The materials here cited as catalysts are numerous and involve as basic substance principally iron oxide in admixture with one or more substances acting as promoters of the activity of the iron oxide. Chromium, nickel, aluminium, thorium, zinc, lead, uranium, and other oxides are cited in this connection. A later patent[1] returns to the claims of B.P. 27955/1913, amplifying them by claiming, for use as catalysts, oxide, hydroxide, and carbonaceous iron ores employed either in bulk or brought into suitable form by powdering and admixture with binding agents. The minerals employed should preferably be free from sulphur, chlorine, phosphorus, and silicon, though small amounts of these are said to be permissible. It is insisted, with regard to the production of all these catalysts, that high temperatures should be avoided in the course of preparation and a limit is set at preferably below 650°. It is obvious that such limitations exclude from use the oxide of iron obtained by the roasting of pyrites ores. The utilisation of this material for catalytic preparations is the subject of a patent by Buchanan and Maxted,[2] who claim the use of the oxide of iron obtained from sodium ferrite as catalyst. The material is prepared by fusion of burnt pyrites with sodium carbonate at elevated temperatures, followed by lixiviation of the mass thus obtained. The mass of iron oxide thus obtained and containing some undecomposed ferrite is claimed to give good conversion at moderate temperatures. A succeeding patent of Buchanan and Maxted[3] claims for the use of metallic couples as improved catalysts. Thus, by reduction of the iron oxide obtained in the manner cited in the previous patent and by immersion of the iron thus obtained in a solution of copper salts a metallic iron–copper couple is obtained with which improved conversion at increased velocities is claimed.

It can readily be shown by means of small scale experiments that many of the catalytic materials cited in this patent literature are capable of facilitating the establishment of the water-gas equilibrium at temperatures from 400–600° at rapid velocities of passage over the catalytic material. The actual material used, therefore, in technical operation

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[1] B.P. 16494/1914.

[2] B.P. 6476/1914.

[3] B.P. 6477/1914.

will depend on factors such as robustness of catalytic material and durability towards impurities in the raw materials for manufacture. That such factors are capable of successful regulation is evident from the fact that plant for the technical operation of the process and the provision of suitable catalytic material was offered for sale early in 1914 by the Berlin Anhaltische Maschinenbau Aktien Gesellschaft, acting as plant erectors for the process as operated by the Badische Co. It is probable that the contact material employed is a suitably prepared oxide, hydroxide, or carbonate ore of iron. The lay-out of the plant will probably be somewhat as follows: Water-gas, generated in an ordinary water-gas plant, is mixed with a measured quantity of low pressure steam. The mixture passes through a series of heat interchangers in which it is heated up to reaction temperatures by means of the outcoming gases passing through the exchangers in the reverse direction. The gases pass from the heat exchangers direct to the reaction chamber (Fig. 17) passing round the outside of the catalyst mass to the top of the same and down through the material, passing thence direct to the heat interchangers and so on to the condensers. The temperature employed and the velocity of gas flow will be governed by the efficiency of the catalyst employed.

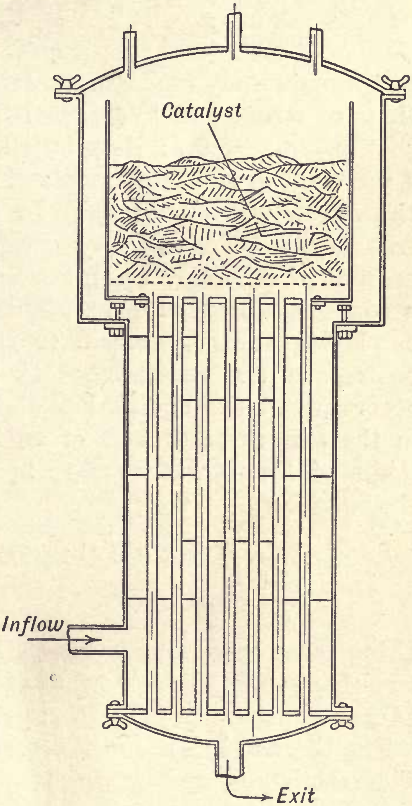

FIG. 17.

Assuming a working temperature of 500° and a catalytic agent capable of producing equilibrium at rapid gas velocities, it is interesting to note the products to be obtained from a commercial blue water-gas containing say 40 per cent. of carbon monoxide. At 500°,

$$k = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}$$

is approximately equal to 0·1, so that with equal concentrations of steam and hydrogen in the exit gases it is obvious that $p_{CO}/p_{CO_2} = 0{\cdot}1$; that is, there would be approximately 4 per cent. of carbon monoxide in the residual products when the steam was eliminated. In practice it is customary to reduce this percentage by employing excess of steam, the amount of reduction being governed by the amount of steam used. Apparently, the best economic balance is secured by employing sufficient steam to reduce the carbon monoxide content of the residual gas to 2 per cent. This involves, according to the equilibrium data, a steam : hydrogen ratio in the exit gases of 2 : 1 or an initial ratio of water-gas to steam of 1 vol. water-gas to $2\frac{1}{2}$ vols. of steam according to the equation:

$$\underbrace{H_2 + CO}_{\text{water-gas}} + 5H_2O \rightleftarrows 2H_2 + CO_2 + 4H_2O.$$

Using these approximate quantities, a typical analysis of the resulting gas will be somewhat of the order $H_2 = 65$ per cent., $CO_2 = 30$ per cent., $CO = 2$ per cent., N_2, etc., 3 per cent.

The thermal balance of the process may now be considered. The reaction occurring,

$$CO + H_2O \rightarrow CO_2 + H_2,$$

is exothermic, 10,000 calories being liberated per molecule of carbon monoxide converted. With good heat exchangers capable of yielding a 75 per cent. heat regeneration, the evolution of heat is sufficient to cover all conduction and radiation losses. Only at starting up is preheating requisite, for which purpose water-gas may be burnt. Subsequently, the mixed water-gas and steam pass through heat exchangers in which they are brought to the reaction temperature of about 500° by means of the heat of the exit gases passing in the reverse direction and leaving the heat exchangers at a temperature of approximately 100°. With such a procedure, the process is continuous, a factor of considerable advantage as compared with other processes of hydrogen production.

The economy of the process may be illustrated from another point of view. Consideration of the reaction equation will show that, theoretically, for the production of one volume of hydrogen, one volume of water-gas is required. In practice, it is claimed that 1·1 volumes of water-gas are sufficient. This is in marked contrast to the conditions obtaining in the steam–iron process, in which from 2 to 4 volumes of water-gas are required, according to practical experience, for the production of 1 volume of hydrogen. As regards the economy of steam in the process, it must also be observed that although an excess of steam is required in this process to decrease the final carbon monoxide content, the steam consumption is much less than in the intermittent steam–iron process, in which, as at present employed, as much as three or four times the theoretical amount of steam required is employed for the production of unit volume of hydrogen. A further advantage of the process exists in that crude water-gas may be employed, no special purification other than the removal of mechanical impurities, such as flue dust, being required. This economy is realisable owing to the fact that all the organic sulphur compounds present in the gas are converted catalytically into sulphuretted hydrogen. This process of sulphur conversion is interesting in other connections and is dealt with in more detail elsewhere in this book. The sulphuretted hydrogen formed in this manner together with that originally present in the gas can readily be removed from the resulting gas mixture along with the carbon dioxide. Obviously, therefore, the hydrogen obtained, being sulphur-free, is especially suitable for certain catalytic operations, as, for example, fat-hardening.

With efficient catalysts comparatively high space-time-yields of residual gas may be obtained. This results, in technical practice, in extraordinary economy of space. It has been computed that the space required for the catalytic process would be roughly one-fifth of that required for the steam–iron process with its unwieldy system of retorts. Single contact-apparatus have been constructed with a capacity of 35,000–40,000 cubic feet per hour in an area of about 20 by 30 feet.

The disadvantages associated with the catalytic process may be enumerated. In the first place, there is the removal of the carbon dioxide, which forms upwards of 30 per cent. of the exit gases from the condensers. Actually this is carried out in practice by a system of counter-current water washing under pressures of about 30 atmospheres. The system is well tried and yields hydrogen with a carbon dioxide content of less than 1 per cent., which may be subsequently removed by lime or alkalis. If the hydrogen has afterwards to be used in the compressed state, the compression costs are negligible. Large quantities of water must necessarily be conveniently to hand, however, for the operation of the process. Part of the energy necessary for pumping the water is recoverable by making the issuing water work an appropriate motor. By means of a Pelton wheel arrangement, 30 to 50 per cent. of the energy may be recovered. Simultaneously with the carbon dioxide, sulphuretted hydrogen is also removed. A certain loss of hydrogen occurs during the process of water-washing, presumably of the order of 10 per cent.

The removal of the unconverted carbon monoxide forms a second obstacle to the utilisation of the catalytic process. Numerous methods have been suggested for effecting this. Certain processes involve methods of absorption, for example, by ammoniacal cuprous salts under pressure. The conversion of carbon monoxide to sodium formate by hot caustic soda solutions under pressure has also been utilised for removal. The gases when freed from carbon dioxide and sulphur compounds are also sufficiently pure to enable one to remove the carbon monoxide by conversion at the expense of hydrogen to methane, using a nickel catalyst. The Badische patent [1] previously cited reduces the monoxide content of the gas by repetition of the main catalytic process under pressures of 4–40 atmospheres. It is obvious that the particular process

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[1] B.P. 26770/1912.

adopted may be governed by various factors operating to determine the choice.[1]

For certain purposes a further disadvantage of the catalytic process lies in the presence in the final hydrogen of the inert gases, *e.g.*, nitrogen, methane, etc., present in the original water-gas. For ammonia synthesis, the presence of nitrogen is no disadvantage. In other catalytic operations, it may act as a diluent, and in circulating systems tends—as does methane also—to accumulate in the gaseous system and so finally bring about a stoppage in the process for the rejection of the diluted hydrogen, or a constant loss of spent gas by continuous removal from the circulatory system.

In spite of these disadvantages, it would seem that the continuous catalytic process is the cheapest and most promising of the processes for large-scale hydrogen production. It is a process also which still offers considerable possibilities for development and improvement, mainly in the treatment of the gases obtained from the contact mass. The efficiency of the process up to this stage may be regarded as already very high.

The problem of removal of the large quantities of carbon dioxide obtained by catalytic conversion of water-gas and steam is the object of another series of patented processes employed upon a technical scale by the Griesheim Elektron Co.[2] The catalytic material is lime suitably activated by admixture of substances like oxide of iron. Operating at temperatures of 400–500°, conversion to carbon dioxide and hydrogen of the water-gas and steam is readily attained. The lime at these temperatures absorbs the carbon dioxide, yielding carbonate, since only above 600° does the dissociation pressure of calcium carbonate become marked.[3] Absorption of the carbon dioxide disturbs the equilibrium which otherwise would prevail, and so the carbon monoxide is thereby more completely removed. Also, the resulting gas does not contain the large quantities of carbon dioxide obtained in the process

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[1] A recent address (Dec., 1918) by Rideal and Taylor to the Society of Public Analysts indicates that carbon monoxide, even in the presence of large quantities of hydrogen, may be oxidised to carbon dioxide by preferential combustion with air or oxygen in the presence of suitable catalysts.

[2] B.P. 2523/Feb. 1909.

[3] Johnston, *J. Amer. Chem. Soc.*, 1912, **32**, 946.

previously considered. On the other hand, it is obvious that owing to the conversion of the lime into carbonate the process is necessarily discontinuous, the lime requiring regeneration by heating to more elevated temperatures. The employment or rejection, therefore, of such a process as an alternative to the catalytic process previously considered hinges on the economy of the regeneration of the lime catalyst as against the process of water-washing under pressure. It will be obvious that for a large-scale hydrogen plant the lime required will be enormous, of the order of 100lb. of lime for 1,000 cubic feet of water-gas containing 45 per cent. of carbon monoxide, assuming that as much as half the lime may be converted to carbonate without impairing its ability to remove the carbon dioxide from the gases produced. It is doubtful whether the expense of regeneration of such quantities of lime would compete in a large technical unit with the continuous system of removal of carbon dioxide by counter-current water-washing. Disintegration of the lime during the process also forms a further disadvantage in practical operation.

The original patents for the lime process were due to Tessie du Motay (1880). The improvement of the Griesheim Elektron Co., which consisted in the addition of 5 per cent. of iron powder to act as an accelerator was studied theoretically by Engels,[1] who found that equilibrium conditions could be obtained at markedly increased velocities of passage of the steam–water-gas mixture when such activators were present. It is obvious that the addition of the iron tends to promote the water-gas reaction as in the continuous catalytic process detailed above and therefore, also, promotes the attainment of equilibrium with the lime. Doubtless, too, it would be found that the active catalysts (iron oxide with promoters), of the continuous process would also accelerate considerably the lime process. Further, a method of procedure should be possible in which the steam–water-gas mixture passed first at 400–500° over an efficient catalyst for the water-gas reaction, then over lime in a second chamber maintained at the same temperature to remove the carbon dioxide, and finally over a further mass of the original catalytic material in which the residual carbon monoxide should be further

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[1] Dissertation, Karlsruhe, 1911.

converted by steam to carbon dioxide, leaving only minimal quantities of carbon monoxide in the hydrogen obtained.

According to Mertz and Weith[1] carbon monoxide and steam react when passed over soda-lime at temperatures of 300° and upwards. This method of manufacture of hydrogen has been suggested for technical operation by the Société générale des Nitrures of Paris.

An alternative series of processes for the production of hydrogen–carbon dioxide mixtures from steam and coke are embodied in the patent claims of Dieffenbach and Moldenhauer. Instead of employing catalytic agents to bring about the water-gas reaction, these claimants propose to facilitate, by addition of catalysts, the reaction between coke and steam, so that it may be carried out at such low temperatures that the products of interaction are principally carbon dioxide and hydrogen. In B.P. 7719/1910, the addition of an alkaline hydroxide or salt, and especially a silicate, is suggested to enable the reaction between coke and steam to be effected within the temperature interval 550–750°. In B.P. 7720/1910, the use of alkalies and alkali salts is suggested. The use of both alkali and lime, it is stated,[2] still further decreases the temperature at which steam and coke will react with rapidity. Whether such proposals have found technical application is not known to the authors.

The steam–iron process of hydrogen manufacture.—As outlined in the introductory paragraphs of this chapter, the production of hydrogen by the action of steam on heated iron is already largely carried out in the industry. The main reaction which occurs may be represented by the equation :

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

By reduction, usually with water-gas, of the oxide of iron thus obtained, the iron may be regenerated and the cycle of operations repeated.

The original patents for the process are very old ; thus, for example, in B.P. 593/1861, Joseph Jacob claims the commercial production of hydrogen by the action of steam on iron filings or borings, or on iron crushed, ground, or pulverised. The heat of the retorts was to be maintained

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[1] *Ber.*, 1880, 13, 719.

[2] B.P. 8734/1910.

by combustion of a portion of the hydrogen produced; the iron after oxidation was to be discharged from the retort.

The alternate reduction and steaming process was patented by Lewes.[1] Hills and Lane[2] and Hills and Monteux[3] utilise this principle in specially designed apparatus for commercial production. The earlier types of plant have been considerably modified in detail as a result of accumulated experience, but the principle of operation remains substantially the same. Further economies of operation are claimed in the numerous patented details of Messerschmidt.[4]

A modern plant for production of hydrogen by the steam-iron process, operating on the same principle, consists of a series of units each containing three sets of retorts generally with twelve retorts to each set. The retorts are from 9 to 12 feet long and from 9 to 12 inches in diameter. It is found in practice that the reduction phase of the cycle occupies a longer period of time than the steaming phase, so that the retorts are operated in such a way that one set is being oxidised by the steam with production of hydrogen whilst the other two sets are reducing. In this way, a reduction period for each retort twice as long as the oxidation period is obtained. The length of the steaming periods vary according to practice from ten to thirty minutes. Reduction is effected by means of water-gas carefully purified from "free" sulphur (H_2S) by means of bog-iron ore. To prevent deposition of carbon in the retorts during reduction, steam is sometimes added to the water-gas, or alternatively a water-gas comparatively rich in carbon dioxide is employed.[5] A considerable excess of water-gas is ordinarily employed for reduction, the excess being burned, after admixture with air, on the outside of the retorts, in order to maintain the necessary temperature. On the other hand, ordinary producer gas is being used in certain plants to maintain retort temperatures. The actual working temperature employed varies in practice between 600° and 850°, the purity of the product desired governing the working conditions.

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[1] B.P. 20752/1890, and B.P. 4134/1891.

[2] B.P. 10,356/1903.

[3] F.P. 386991/1908.

[4] See *J. Soc. Chem. Ind.*, 1914, 33, 313.

[5] B.P. 12698/1915.

According to the patent specification of Lewes, iron borings may be employed for the reaction. Since the two phases of the process are, however, mainly surface actions, or at most penetrate but little into the interior of the material, recent practice has resolved itself into the substitution, for metallic iron, of iron in a porous or spongy condition which will offer a maximum of surface for a minimum of volume. The iron is therefore generally obtained by reduction of a mineral oxide or from carbonate ores such as spathic iron ore by reduction of the mass obtained after ignition and loss of carbon dioxide. In this way, material possessing both porosity and resistance to disintegration is readily obtained. Roasted pyrites from which all sulphur and the volatile metals have been removed has also been proposed as the reaction material.[1] All such materials show a greater or less tendency to lose their activity with repeated oxidation and reduction, and research into the causes thereof conducted on the large technical scale have shown it to be in part due to fritting of the surface. Part of the loss in activity is due to deposition of foreign bodies such as carbon, sulphur, etc., in the mass, but these may be removed by periodical heating in a current of air. The fritting, however, is permanent, and consequently many suggestions have been put forward to counteract this difficulty. They consist chiefly in the admixture with the iron of bodies which may either render the iron less fusible and less liable to soften with the temperatures employed, or which may catalytically assist the interaction of steam with iron so that good yields of gas may be obtained at lower temperatures than would normally prevail. Thus Messerschmidt proposes[2] the use of natural ores of manganese and of manganese and iron to attain lower reaction temperatures. Dieffenbach and Moldenhauer[3] claim the use of alloys of iron with manganese, chromium, tungsten, titanium, aluminium, or other similar elements, as well as mixtures of the oxides briquetted or in other suitable form. The Badische Anilin- & Soda-Fabrik[4] propose iron oxide fused with refractory oxides such as zirconia and magnesia or with silicates. Jaubert[5] suggests the use of briquettes of iron oxide admixed

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[1] B.P. 7849/1909.
[2] F.P. 461480/1913.
[3] D.R.P. 233347/1910.
[4] F.P. 440780/1912.
[5] F.P. 418312/1909.

with fireclay, pumice, magnesia, and small amounts of the oxides of manganese, chromium, copper, and lead.

The gas obtained by the steam–iron process contains, after removal of small quantities of carbon dioxide and hydrogen sulphide by means of lime purifiers, upwards of 98 per cent. of hydrogen. With careful control a content of hydrogen as high as 99·75 can be continuously maintained without considerable increase in cost of production. Higher purity still, averaging 99·85–99·95 per cent. of hydrogen, can be maintained by extraordinary precautions as to scavenging and by use of an elevated temperature coupled with frequent aeration of the contact mass. Naturally, this increases considerably the cost of the gas owing to loss of yield, decreased activity of the iron due to fritting, and wear and tear of retorts at the high temperatures.

The main impurity of the gas is carbon monoxide resulting from interaction of the steam and carbon deposited in the iron during the reducing phase. This carbon results from the catalytic decomposition of the carbon monoxide [1] in the presence of iron according to the equation :

$$2CO \rightleftharpoons C + CO_2$$

In the steaming phase this carbon reacts with the steam to form carbon monoxide, and dioxide, the concentration of steam present determining to a considerable degree the relative quantities of each in the issuing gas. As stated, the carbon dioxide is removed by means of lime purifiers, the carbon monoxide passing on with the hydrogen. Since the carbon in the iron mass is only incompletely decomposed by the steam, it gradually accumulates in the material and must therefore be occasionally removed by means of a hot air current.

The efficiency of the steam–iron process leaves much to be desired. Only during the initial minutes of steaming is the yield of hydrogen anything approaching quantitative. In the latter stages of the period of oxidation, the main bulk of the steam passes on unchanged, with the total result that

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[1] For equilibria, see Boudouard, *Compt. rend.*, 1900, **130**, 132 ; Rhead and Wheeler, *J. Chem. Soc.*, 1912, **101**, 831.

for the production of one volume of hydrogen as much as three to five volumes of steam are frequently employed. Also, the maintenance of the temperature of the reaction mass consumes a considerable portion of the reducing gases, the residual gases after passing through the retorts being burned on the outside of the retorts. Naturally, the large excess of steam employed does not make for efficiency on the thermal balance of the process. Endeavour is made to economise in regard to heating by Jaubert.[1] The oxidation with steam is exothermic. According to Jaubert, reduction of magnetic oxide of iron by carbon monoxide is slightly exothermic (1 kg. cal.) whereas that by hydrogen is strongly endothermic (18·2 kg. cal.). Jaubert finds that if the water-gas used for reduction be thoroughly purified, especially from sulphur compounds, a more reactive water-gas is obtained, operating energetically at a much lower temperature and with such a preponderance of reduction by carbon monoxide that it is possible almost to suppress the special heating of the retorts. The simple combustion around the retorts of the small quantity of the residual gases, rich in hydrogen, is sufficient to maintain the furnace at the requisite temperature.[2] Many of the patent devices of Messerschmidt have similar economies of thermal energy in view. It should be possible with a system thoroughly reorganised from the chemical and engineering points of view to raise the efficiency of the steam–iron process to a considerable degree. If such were attained it would easily be the process most preferred, since it has the very considerable advantage that the product is hydrogen free from any large amounts of foreign gases.

The Bergius hydrogen process.—The patents of Bergius,[3] relative to the manufacture of hydrogen by the action of liquid water, at elevated temperatures and therefore at high pres-

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[1] F.P. 419667.

[2] The thermal data relative to the reduction of the oxides of iron by water-gas are sufficiently uncertain to merit special investigation. The data of Bauer and Glaessner, *Zeitsch. physikal. Chem.*, 1903, **43**, 358, on carbon monoxide reduction, conflict with the later data of Schenk, *Ber.*, 1905, **38**, 2132, 1907, **40**, 1704; van Royen, *Diss. Bonn.*, 1911; Levin and Köster, *Nernst Festschrift*; Halle, 1911; Falcke, *Zeitsch. Elektrochem.*, 1916, **22**, 160, nor are these reconcilable with data on reduction by hydrogen, *e.g.*, Chaudron, *Compt. rend.*, 1914, **159**, 237, nor with the thermal data of the water-gas equilibrium.

[3] D.R.P. 259030/1911, 254593/1911, and 262831/1912.

sures, upon carbon or iron disclose certain interesting details as to the use of catalytic accelerators.

Bergius found that, at a temperature of 300° and at a pressure sufficient to keep the water liquid, carbon reacted almost exclusively with water to form a mixture of carbon dioxide and hydrogen according to the equation :

$$C + 2H_2O \rightarrow CO_2 + 2H_2.$$

The addition to the water of small quantities of thallium salts was found to promote the reaction catalytically.

Employing iron, the corresponding reaction with liquid water also took place at the low temperature of 300°. Only in the initial stages of the reaction was heat required, the exothermicity of the reaction being sufficient to maintain the gas evolution. Pressures of 100 atmospheres or more were generated in the system and were reduced to the desired extent by occasionally blowing off the gas through a valve into cylinders in which the hydrogen could be stored already compressed. Catalytic acceleration of the reaction was secured by dissolving in the water neutral salts, as, for example, sodium chloride, or acids, or by use of metallic couples such as iron–copper, or by the presence of a second metal such as nickel or platinum.

The Bergius iron–water process should be cheap and useful for small-scale hydrogen production under pressure where an expensive equipment is not possible. Regeneration of the finely divided iron metal employed can be effected by means of water-gas, producer-gas or carbon at high temperatures.

Hydrogen production by catalytic decomposition of hydrocarbons.—In general, the saturated hydrocarbons, when subjected to a sufficiently high temperature, decompose into their elements, the carbon being deposited in an extremely fine state of division, hydrogen being simultaneously produced.[1] The temperature required for decomposition varies with the stability of the compound. Thus, methane dissociates rapidly only at 1200° to 1300°, its presence in a water-gas mixture being evidence that at the slightly lower temperature of water-gas manufacture the velocity of decomposition is

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[1] Mayer and Altmayer, *Ber.*, 1907, 40, 2134.

comparatively low. On the other hand, acetylene decomposes at much lower temperatures, Pictet,[1] effecting decomposition by passage through tubes heated initially to 500°. Since heat is evolved upon the decomposition of acetylene, the reaction continues automatically when once started. This process is generally applicable to endothermic hydrocarbons.

Numerous patented processes exist for the production of hydrogen by this method, the variations being, in the main, modifications for the better operation in technical practice. Thus the Carbonium Co., of Friedrichshaven, decompose acetylene under pressure by explosion with an electric spark. The hydrogen obtained is of high purity and has been employed for the filling of Zeppelins. The cost is, however, somewhat considerable, unless the lamp-black can be marketed. The pressures employed may be as much as 6 atmospheres.[2]

The decomposition of the light petroleum hydrocarbons is the subject of patents by Lessing[3] and by Pictet,[4] in which temperatures from 1000–1350° are suggested. It is obvious that technical operation at such high heats is a matter of considerable difficulty and it is not surprising that extended application has not yet been recorded. Recent work on the cracking of heavier hydrocarbon vapours will doubtless contribute greatly to the development of technique in this direction.

To bring about the decomposition of hydrocarbons at lower temperatures interaction with steam has been employed both with and without catalytic contact material. Pictet[5] produces thus carbon monoxide and hydrogen from hydrocarbon vapours and steam at high temperatures. The Badische Anilin- & Soda-Fabrik[6] suggest a refractory oxide such as magnesia impregnated with nickel oxide as catalyst for this process, at a temperature of 800°. Dieffenbach and Moldenhauer[7] use as catalyst wire gauze of nickel, cobalt, platinum, etc., for the same reaction ensuring by the employment of the catalyst in such form, a very short time of contact and thereby a sudden cooling of the reaction products. In this

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[1] F.P. 421839/1910.
[2] Machtolf, D.R.P. 194301/1909.
[3] B.P. 15071/1909.
[4] B.P. 13397/1911.
[5] B.P. 14703/1911.
[6] B.P. 12978/1913.
[7] D.R.P. 229406/1909.

way the carbon dioxide formed has little opportunity to be reduced to carbon monoxide.

Coke rendered white hot by an air blast has been proposed by the Berlin Anhaltische Maschinenbau A.G.[1] and by Ellis[2] as contact material for the production of hydrogen from paraffin hydrocarbons.

It should be possible with the aid of catalytic contact material to bring about the interaction of hydrocarbons with carbon dioxide to yield carbon monoxide and hydrogen, whence pure hydrogen could be obtained by processes described above. With unsaturated hydrocarbons this is apparently not difficult. A solution of the problem with the lower paraffins should yield to a systematic search for suitable catalytic material.

HYDROGENATION

The systematic investigation of the problem of hydrogenation was undertaken at the close of the nineteenth century by Sabatier and his co-workers, of whom Senderens may principally be mentioned. Isolated observations had earlier been made and recorded concerning interaction of substances with hydrogen in the presence of a catalytic material. Generally, finely divided platinum was the agent employed. Its activity in promoting oxidation as manifested in the early work of Davy and Döbereiner had led to its trial in many other directions, sometimes with success. Thus the catalytic reduction to ammonia of oxides of nitrogen by means of hydrogen in the presence of platinum sponge was recorded by Kuhlmann in 1838.[3] Carenwinder[4] showed its catalytic effect in promoting the combination of hydrogen and iodine. Applied to organic reactions, it was observed by Debus[5] that platinum black assisted the reduction of hydrocyanic acid to methylamine, and that ethyl nitrite could be transformed by means of hydrogen into ethyl alcohol and ammonia. The catalytic addition of hydrogen to unsaturated hydrocarbons and their transformation to saturated hydrocarbons was demonstrated

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[1] B.P. 2054/1914.

[2] U.S.P. 1092903/1914.

[3] *Compt. rend.*, 1838, **17**, 1107.

[4] *Ann. Chim. Phys.*, 1852, (iii), **34**, 77.

[5] *Annalen*, 1863, **128**, 200.

by De Wilde in 1874,[1] platinum black being employed as agent.

By the researches of Sabatier and his assistants the catalytic method of hydrogenation has been generalised. From 1897 onwards, in a succession of researches published in the *Comptes rendus* of the Paris Academy of Sciences, by systematic application of the principle to the most diverse organic materials and employing various metals as catalytic agents, the wide applicability of hydrogenation has been made clear. The reactions have been studied generally in the vapour phase, volatile organic liquids being for the most part the materials employed in the investigation. Finely divided metals have formed the catalytic agents, and of these, nickel, obtained freshly from the oxide by reduction, has proved to be the most efficient. The other elements which have found application are cobalt, iron, copper, platinum, and the platinum metals generally.

The simplicity of the studies carried out by Sabatier and his collaborators is striking. The procedure consisted essentially in passing hydrogen intermingled with vapours of the material to be investigated through a tube containing the finely divided catalytic agent maintained at a controllable temperature, the products of reaction being suitably collected on emergence from the heated tube.

It was found to be essential that the hydrogen employed should be completely free from all impurities. Traces of sulphuretted hydrogen, of phosphine, arsine, and hydrogen chloride were found to act as catalyst poisons. Hydrogen, obtained by electrolysis and subsequently freed from traces of oxygen and moisture, was therefore largely employed, since by this process the other impurities could readily be avoided.

The preparation of the catalytic mass proved to be the matter of chief importance apart from the purity of the materials employed. In the majority of cases studied by Sabatier, nickel was the agent used, and so certain details relative to its preparation and properties are apposite. It was prepared by reduction, with hydrogen, of the oxide, generally placed in position in the tube in which the reaction

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[1] *Ber.*, 1874, 7, 352.

to be studied was effected. Chlorine, bromine, and iodine are to be stringently avoided in the materials from which catalytic nickel is prepared, as these are poisons. Sulphate may in certain cases yield good results. The activity of the reduced nickel varies greatly with the nature of the oxide and the conditions of reduction. A light, bulky oxide yields an active catalyst, the more active the lower the temperature at which reduction occurs. A compact oxide yields a catalytic mass much more sluggish in its activity. The temperature of reduction varied between 200° and a red heat.

Associated with the activity of the catalyst is its durability in action. Normally, the more active catalyst has a short life, the more robust as regards durability being less active. In every case the catalytic mass shows an initial period of sluggish action gradually improving to a maximum and normal catalytic activity. This latter is generally a quite long period, and its termination may be attributed to the action on the nickel of minute traces of foreign materials deposited in the mass from the reacting substances. Small traces of sulphur, chlorine, bromine, or iodine are sufficient in time to produce the final period of diminishing activity followed by complete inaction. Decreasing efficiency may also be attributed in part to a change in the physical state of the catalyst, whereby, due to local overheating or to the prolonged effect of moderate temperatures, transformation from an open porous mass to a more compact form ensues.

Cobalt prepared in the same manner as nickel behaves similarly but it is, normally, less active and less robust. Reduced iron requires higher temperatures than does nickel in the corresponding reactions; but in many cases it is not applicable. The difficulty of securing complete reduction of the iron oxide constitutes a further drawback. Copper is readily prepared in a very active condition by reduction of the oxide at low temperatures. It is, however, not so widely applicable as is nickel, and also shows great variability in action according to the manner of its production. Platinum black, the agency first employed for catalytic hydrogenation, can be used in numerous instances. It is superior in activity to copper, but less efficient than nickel. The state of division largely determines its activity. Also, it is rapidly rendered inactive in use. Finely divided palladium, which, as is well known, occludes large volumes of hydrogen, is a very active catalytic agent, operating at very low temperatures. Thus, carbon monoxide is hydrogenated to methane in the cold in the presence of palladium. Naturally its use is restricted by its costliness.

Hydrogenation in the presence of metallic catalysts may conveniently be classified, according to Sabatier,[1] in three groups

(1) Reductions with simultaneous fixation of hydrogen.
(2) Fixation of hydrogen by unsaturated compounds.
(3) Hydrogenation with accompanying rupture of the molecule.

A *résumé* of the typical examples of these three groups, as cited by Sabatier, is given in the following, together with a fuller description of those reactions having a more technical significance.

REDUCTIONS WITH SIMULTANEOUS FIXATION OF HYDROGEN

Oxides of nitrogen.—Nitric oxide is readily reduced in presence of nickel at 180° with formation of ammonia and water, the equation being

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O.$$

The ammonia formed has a tendency to combine with unchanged nitric oxide to form nitrogen and water :[2]

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O.$$

This reaction is of importance in the process, elsewhere discussed (p. 92), of ammonia oxidation, as its occurrence in that process may diminish considerably the efficiency of such catalytic oxidation.

Nitrogen peroxide is reduced by hydrogen in presence of nickel at 180°. The ammonia formed interacts with unreduced

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[1] "La Catalyse en Chimie Organique," 1913.

[2] Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 278.

oxides, and ammonium nitrite and nitrate are produced. Further hydrogenation yields ammonia and water :

$$2NO_2 + 7H_2 \rightarrow 2NH_3 + 4H_2O$$

With high concentrations of nitrogen peroxide the reaction is very energetic, producing incandescence in the neighbourhood of the contact mass and frequently giving rise to explosions.

Similarly with the vapours of nitric acid, at 200° ammonium nitrate is produced, whilst, at 350°, nitrogen, ammonia, and water are the reaction products.

Organic nitro-compounds.—The aliphatic nitro-compounds are readily hydrogenated with nickel to the corresponding amine :

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O,$$

but at more elevated temperatures the hydrogenation may proceed still further. Thus, nitromethane yields methylamine, but may partially yield methane and ammonia[1] :

$$CH_3NO_2 + 4H_2 \rightarrow CH_4 + NH_3 + 2H_2O$$

Similarly, aromatic nitro-compounds yield the corresponding amines. Further hydrogenation at higher temperatures yields the aromatic hydrocarbons and ammonia, whilst more elevated temperatures of reaction may carry the hydrogenation of the aromatic hydrocarbon yet further, yielding methane. Thus, in successive stages, nitrobenzene will yield aniline and water, then benzene, ammonia, and water, and with complete hydrogenation methane, ammonia, and water. By controlling the temperature, the two latter reactions may be practically suppressed, and good conversion of nitrobenzene to aniline obtained.[2]

Dinitro-derivatives yield the corresponding diamines. Nitrophenols yield amidophenols with side reactions yielding ammonia, phenol, and water, and some aniline. Nitrous ethers yield the corresponding amines by reduction in presence of nickel, just as do the isomeric nitro-compounds. A production of the secondary and tertiary amines always occurs, the secondary amine generally being produced in the greatest amount. Gaudion[3] explains his results with these compounds

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[1] *Compt. rend.*, 1902, **135**, 226.

[2] Senderens, F.P. 312615/1901.

[3] *Ann. Chim. Phys.*, 1912, (viii), **25**, 129.

by assuming isomerisation of the nitrous ethers in presence of the catalyst.

Oximes on catalytic reduction yield primary and secondary amines. The amides of the fatty acids yield the corresponding primary amine and water with some formation of the secondary amine by rupture of the molecule and simultaneous production of ammonia.

Halogen derivatives.—Direct reduction of halogen aromatic compounds is possible, employing finely divided nickel as catalyst. The ease of reduction is a function of the compound. The presence in the ring of substituent groups such as methyl or hydroxy-radicals facilitates reduction. In general, the chloro-derivatives are the most easily reduced. The bromo-derivatives are less easily reduced and the iodo-compounds least of all. This order is what would be expected in view of affinity relationships between hydrogen and the respective halogens. On an intermediate compound theory of catalysis, also, the same order would be forecasted, since nickel chloride is readily reduced by hydrogen at 270° ; whereas the bromide is less easily reduced and the iodide practically not at all at such temperatures.

In exemplification of the catalytic reduction, the following reactions will serve. At 270° monochlorobenzene is rapidly hydrogenated, benzene being formed. A certain quantity of diphenyl is, however, simultaneously formed, due possibly to the direct action of the metallic catalyst on the chloro-derivative.

Poly-chloro-derivatives yield the reduced products in successive stages. Thus dichlorobenzene gives successively monochlorobenzene and benzene. From hexachlorobenzene a mixture of the tri-, di-, and mono-chlorobenzenes is obtained.

The chlorotoluenes are more readily reduced than the chlorobenzenes. Trichlorophenol gives a mixture of 70 per cent. of phenol and some monochlorophenols. Chloroanilines readily yield the corresponding hydrochloride. Chloronitro-compounds suffering simultaneous reduction of the chlorine and nitro-groups also yield the hydrochlorides of the corresponding amine.

Oxygen-containing carbon compounds.—A number of oxygen-containing carbon compounds may be catalytically reduced with simultaneous fixation of the hydrogen. Thus ethylacetoacetate is converted to ethyl butyrate according to the equation :

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COO{\cdot}C_2H_5 + 2H_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COO{\cdot}C_2H_5 + H_2O.$$

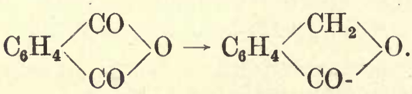
This reaction is always accompanied by side reactions. A split of the molecule may occur ($CH_3{\cdot}CO{\cdot}CH_2$–and–$COO{\cdot}C_2H_5$), the products yielding further reduced substances, the former acetone and secondary propyl alcohol, the latter ethyl formate, which decomposes under the reaction conditions to ethyl alcohol and carbon monoxide. This latter may be transformed to methane during the reaction. Alternatively, condensation of the molecule may occur as a side reaction, catalytically assisted by the nickel. The hydrogen does not function in the change, the products of condensation being dehydracetic acid and ethyl alcohol, according to the equation :

$$2(CH_3{\cdot}CO{\cdot}CH_2{\cdot}COO{\cdot}C_2H_5) = (CH_2{\cdot}CO)_4 + 2C_2H_5{\cdot}OH.$$

With nickel of medium activity, aromatic ketones are reduced to the corresponding benzene derivative. Thus acetophenone, $C_6H_5{\cdot}CO{\cdot}CH_3$, yields ethyl benzene. Similarly, aromatic diketones give the corresponding hydrocarbons :

$$C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5 + 4H_2 \rightarrow C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5 + 2H_2O.$$

The anhydrides of dibasic acids give the corresponding lactones. Thus succinic anhydride gives butyrolactone, orthophthalic anhydride the corresponding phthalide, *e.g.*,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O \rightarrow C_6H_4{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O.$$

The phenols and poly-phenols may be reduced to the corresponding hydrocarbons, but the yields are low.

Aldehydes.—Aldehydes on reduction are converted to the corresponding alcohols,

$$R{\cdot}CHO + H_2 = R{\cdot}CH_2{\cdot}OH$$

This reaction is of prime importance in the modern work on the production of synthetic alcohol. As shown elsewhere (p. 250), from calcium carbide as starting point, acetaldehyde may be synthesised, via acetylene, which is catalytically hydrated to yield the aldehyde. Using Sabatier's catalytic hydrogenation process, the aldehyde thus produced may be converted to ethyl alcohol. The reaction is conducted in the presence of reduced nickel at 140°, using dry aldehyde vapour and pure hydrogen. The completeness of the synthesis is limited by the reverse process of dehydrogenation of the alcohol produced, but, with careful control, a conversion of 80 per cent. of the aldehyde is possible in a single passage over the catalyst. Temperature control must also be rigorous owing to the possibility of catalytic decomposition of the aldehyde, which, at 180°, under these conditions is rapidly converted to methane and carbon monoxide,

$$CH_3{\cdot}CHO = CH_4 + CO.$$

The products of reaction, consisting of alcohol, unchanged acetaldehyde, and hydrogen, are collected, and, by a process of continuous fractionation, are separated, the unchanged materials returning to the reaction system.

Oxides of carbon.—Both carbon monoxide and carbon dioxide may be reduced by hydrogen in the presence of metallic nickel. In each case the products of reduction are methane and water, the reactions occurring being representable by the equations :

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

With an active nickel catalyst the reaction with carbon monoxide may commence as low as 180° to 200°, the velocity of reaction increasing rapidly with the temperature, so that at 250° the conversion is practically complete. With carbon dioxide the reaction commences at a somewhat higher temperature, towards 230°, and is rapid above 300°. It has been suggested that the dioxide may thus be used as a suitable starting point for the preparation of pure methane. It is necessary, however, to exercise care in the process, otherwise carbon monoxide will be found in the reaction product after removal of the carbon dioxide by alkali. The occurrence of carbon monoxide in the hydrogenated products of carbon dioxide is of interest, and further study of this point should yield information on the precise mechanism of reduction.

With carbon monoxide at temperatures above 250° a second reaction may occur, also catalytically assisted by metallic nickel, as well as by many metallic catalysts, *e.g.*, iron. Carbon monoxide is decomposed, yielding carbon and carbon dioxide according to the equation,

$$2CO \rightleftarrows C + CO_2.$$

The carbon is deposited on the nickel catalyst, rapidly rendering it ineffective catalytically.

The technical application of these hydrogenation processes to the production of illuminating gas has been the object of considerable investigation. A review of this work may therefore here be given.

TECHNICAL SYNTHESIS OF METHANE: THE CEDFORD PROCESS

Elworthy in 1902[1] was the first to apply the process of Sabatier and Senderens to the technical production of methane from carbon monoxide. He employed water-gas as the source of his methane. The gas was freed from carbon dioxide and so much hydrogen added that the theoretical mixture ($CO + 3H_2$) for methane formation was obtained. The conversion was to be effected by passage of the gases over finely divided nickel at 250°. The process was to be exploited by an English company, but technical difficulties, mainly the short life of the catalyst coupled with the death of the patentee, affected the progress of the work adversely and the problem therefore remained unsolved.

Sabatier himself attempted the solution of the problem.[2] At the outset, he sought to reduce carbon dioxide by means of hydrogen at temperatures of 350°. Later, he proposed an alternative process,[3] utilising the decomposition of carbon monoxide to carbon and carbon dioxide which occurs readily at 500° in the presence of a nickel catalyst, together with the observation that the carbon deposited in the mass readily combines with superheated steam to form carbon dioxide and methane. In this manner mixtures of methane, hydrogen,

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[1] B.P. 12461/1902 and 14333/1904.

[2] F.P. 354621/1905.

[3] F.P. 355900/1905.

and carbon dioxide could be produced from water-gas. The reaction could be conducted in the two stages, or, by passage of suitable proportions of water-gas and superheated steam simultaneously over the catalyst at 500° the two reactions could be superimposed. In conjunction with A. Girard, considerable energy was expended in attempting this alternative scheme on economic lines, but presumably without success.

In a later patent,[1] Sabatier returned to the direct reduction process, employing a low temperature water-gas with a high carbon dioxide content and a correspondingly low content of carbon monoxide (12 per cent.). In this way the necessary excess of hydrogen was obtained. The gas after removal of the carbon dioxide was passed first over heated copper to remove impurities and then over the nickel catalyst to convert the mixture into methane and hydrogen.

An alternative method of producing the hydrogen-rich gas necessary for the production of methane was worked out by Bedford in the laboratories of Prof. Erdmann, Halle-a-S., and the technical possibilities of the process were exploited by the Cedford Gas Process Co. in England.

The difficulties in the way of a technical solution of the problem of reduction of carbon monoxide by hydrogen in the presence of nickel may be briefly summarised as follows :

(1) Theoretically, three volumes of hydrogen are required for one of carbon monoxide. In technical practice, it is found that at least five volumes are requisite.

(2) Sulphur-containing gases poison the nickel catalyst.

(3) The decomposition of carbon monoxide to carbon dioxide and carbon may occur with decomposition of the latter on the nickel catalyst resulting in loss of catalytic activity.

The use of low temperature water-gas as suggested by Sabatier to overcome the first difficulty suffers from the disadvantage that considerable quantities of carbon dioxide must be removed, an operation of considerable expense. Alternatively, Elworthy's proposal to admix hydrogen is limited in its application by the relatively high cost of hydrogen. The attainment of the hydrogen-rich gas can, however, be realised by removal of carbon monoxide from water-gas,

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[1] F.P. 400656/1908.

and this is possible by the physical method of liquefaction, making use of the difference in the boiling points of the two constituents ($H_2 = -252{\cdot}5°$; $CO = -190°$). As mentioned elsewhere (see p. 157), this process of liquefaction has been employed by Frank and Caro for the preparation of hydrogen.

By a modification of the method of operation it was found possible so to conduct the liquefaction that at the temperature of liquid air so much carbon monoxide was removed from water-gas that an uncondensed fraction containing 14 per cent. of carbon monoxide was obtained. The liquefied carbon monoxide was vaporised, a portion mixed with the 14 per cent. fraction to bring it up in composition to 17 per cent. and the remainder burned in gas engines to yield motive power to drive the compressors and also to work the pumps necessary to remove all traces of carbon dioxide from the original water-gas. This was accomplished by washing with water and with alkali under pressure, or according to the patent of Behrens and Behrens[1] by alcohol under pressure in a circulatory system.

The adoption of the liquefaction process to obtain the hydrogen-rich gas mixture simultaneously solved the second difficulty in the process. For in the cooling operation it was found that all sulphur compounds were completely removed from the uncondensed portion and remained behind as solids in the carbon monoxide-rich fraction. A gas was obtained so free from sulphur impurities that after the passage of 500,000 litres over 200 grams of reduced nickel the activity of the catalyst was absolutely unimpaired. From other sources, it is possible to confirm this observation as to freedom from sulphur, and it may be stated that as much as 3,000,000 volumes of gas per volume of catalyst may be successfully treated without recording a departure from the quantitative nature of the conversion.

The further difficulty associated with the process, due to carbon deposition, is practically eliminated by use of the gas with five volumes of hydrogen to one of carbon monoxide. The diluent effect of the hydrogen is sufficiently great to prevent decomposition occurring in any marked degree.

For the reduction process it was found that three quartz

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[1] D.R.P. 226942.

tubes,[1] 1·5 metres long and 12 cm. diameter, each containing 200 grams of finely divided nickel, were adequate for the treatment of 400–500 cubic feet of gas per hour. The yield of methane-rich gas thus obtained averaged 200 to 250 cubic feet per hour. The quartz tubes were maintained at a temperature of 280° to 300°. Since the reaction is strongly exothermic,

$$CO + 3H_2 = CH_4 + H_2O + 48{,}900 \text{ cal.},$$

it may readily be shown that with a gas of 17 per cent. carbon monoxide content, the process will maintain itself without the supply of external heat.

In a sixty-hour test run under these conditions the following sample data were collected :

	CO_2.	CO.	H_2.	N_2.	CH_4.	Cal. val. per cub. ft.
(*a*) Composition of the water-gas	3·8	38·3	52·2	5·7	—	288
(*b*) Water-gas freed from CO_2	0	41·0	54·0	5·0	—	—
(*c*) Hydrogen-rich gas	0	13·9	84·3	1·8	—	298
(*d*) Carbon monoxide-rich gas	0	93·2	0·5	6·3	—	325
(*e*) Mixture of (*c*) and (*d*) used for reaction	0	16·3	80·9	2·8	—	298
(*f*) Samples after reduction (1)	0	0	64·8	6·9	28·3	466
(2)	1·4	0·2	60·6	5·8	31·8	488
(3)	0·6	0	61·4	6·2	31·8	490

It was shown that if diminution in activity of the nickel due to carbon deposition occurred, this could be removed by slowing down the stream of gas for a period of time during which the nickel recovered its activity. According to Mayer and Henseling,[2] this is due to interaction of the deposited carbon with hydrogen to form methane.

To avoid carbon deposition, the carbon monoxide content is kept below 17 per cent. Hence a gas with more than 32 per cent. of methane cannot be obtained in one operation. Actually, however, by addition of further quantities of carbon monoxide to the reduced gas, the process may be repeated and a gas containing as much as 76 per cent. of methane may be obtained by successive treatments.

As to the economics of the process, Mayer and Henseling are pessimistic. Erdmann, on the other hand, claims considerable possibilities for the process. It is obvious that a

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[1] Thermal Syndicate, Wallsend.

[2] *J. f. Gasbeleucht*, 1909, **52**, 169, 197.

considerable reduction in volume occurs in the process, so that large volumes of gas must necessarily be treated to obtain a given output. This would militate against its successful utilisation as a source of illuminating gas *per se*. On the other hand, the considerable increase in calorific value per unit volume accompanying the conversion suggest its application as an enriching agent for water-gas produced in gas-works for addition to the ordinary coal-gas supply. This would obviate the use of oil supplies for carburetting water-gas and therefore increase the quantities of such material available for other purposes. There seems to be distinct possibilities of use for a gas with a calorific value averaging 350 B.T.U. capable of production at a figure comparable with that of coal-gas. The product of the Cedford process, it was seen, averages 480 B.T.U. per cubic foot, so that admixture of this with an ordinary water-gas of 300 B.T.U. in equal proportions would yield a gas of calorific value well above the 350 B.T.U. standard. The cost of production, also, should be within the limits of practical consideration. Nevertheless, so far as is known, no considerable technical development has taken place in such direction. Extended familiarity with technical catalytic processes may, however, promote such development along the lines suggested by the above outline or in similar directions, employing other catalytic agents for the production of the methane.

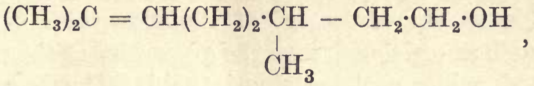
HYDROGENATION OF UNSATURATED COMPOUNDS

By far the greater number of catalytic hydrogenation processes may be classified in this grouping, and in the hardening of oils the utility of the process finds a practical application. Examples of hydrogenation of all types of unsaturated compounds may be given, including compounds containing the ethylene double bond, the acetylene triple bond, the triple and quadruple linkage between carbon and nitrogen, the double bond between carbon and oxygen, the benzene nucleus, and various other unsaturated nuclei.

The ethylene linkage is readily hydrogenated in the presence of metal catalysts. Thus, in presence of nickel, ethylene itself is hydrogenated at temperatures as low as 30°, ethane being the product. The rate of reaction increases with temperature, and is very rapid in the temperature interval 130–150°. If the temperature employed be too high, decomposition of the hydrocarbon, in other words, dehydrogenation, also sets in, with deposition of carbon and liberation of a mixture of ethane, methane, and hydrogen, the two latter in larger quantities the higher the temperatures employed. This behaviour is quite general for all the ethylene hydrocarbons investigated. At the lower temperatures, hydrogenation proceeds more or less quantitatively to the corresponding saturated compounds. At elevated temperatures, decomposition sets in, with formation of simpler hydrocarbons and hydrogen together with carbon and a small proportion of complex liquid hydrocarbons.

The problem of hydrogenation of unsaturated hydrocarbons is allied to the experimental work of Bergius on the action of high pressure hydrogen on coal and tar oils. Experimental investigation shows that, at 400°, and 100 atmospheres hydrogen pressure, hydrocarbon oils result from coal, and that these yield, on distillation, products resembling the paraffin hydrocarbons. The application of catalytic agents to such reactions would seem to offer possibilities of development in a technical direction more promising than the trials conducted in Germany in 1914 without the use of such agents.

Alcohols with a single unsaturated linkage are hydrogenated, with formation of the corresponding saturated alcohol. Thus at 130–170°, in presence of nickel, allyl alcohol yields propyl alcohol. Similarly, citronellol,



$$(CH_3)_2C = CH(CH_2)_2\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2\cdot CH_2\cdot OH,$$

yields the dihydro-derivative.

With aldehydes, conversion to the saturated aldehyde is readily effected, but simultaneous reduction to the saturated alcohol occurs, though at a less rapid rate of reaction. Thus crotonaldehyde gives a 50 per cent. yield of butyric aldehyde and 20 per cent. of butyl alcohol when heated with hydrogen in presence of nickel at 125°.

By adjustment of the temperature of operation, ketones with ethylene linkages can be reduced to the saturated compound without simultaneous reduction of the ketonic grouping. Thus at 160–170° phorone, $(CH_3)_2C = CH{\cdot}CO{\cdot}CH = C(CH_3)_2$, gives di-isobutyl acetone. At 225°, the corresponding secondary alcohol and saturated hydrocarbon appear in the product.

Unsaturated acids are likewise hydrogenated without any action of the acid on the metal catalyst; this is of importance in the technical hydrogenation of oils, since these always contain small amounts of free acids.

The esters and glycerides of unsaturated acids are likewise hydrogenated readily in the vapour phase. For technical operation, however, the discovery that hydrogenation could be effected in the liquid phase obviated the necessity of employing the vapours of the oils, most of which are non-volatile. A considerable industry in the hydrogenation of oils has now been established, the details of which merit extended consideration.

HYDROGENATION OF OILS

The classic studies of Sabatier and Senderens which have just been detailed undoubtedly laid the foundation for the development of the many processes now in technical operation for the hardening of oils by hydrogenation. The problem of oil hardening, briefly stated, consists in the conversion of oils which at the ordinary temperature are liquid into fats which are hard under the same conditions. Chemically expressed, the problem is the transformation, by addition of hydrogen to the molecule, of the glycerides of unsaturated acids, such as oleic acid, into the glycerides of the corresponding saturated acids, such as stearic acid. The hydrogenation is accompanied by the elevation of the melting point of the glyceride. Since the market value of solid or semi-solid fats is intrinsically higher than that of the liquid fats, it is obvious that such a transformation, if effected cheaply, has a large industrial importance in the soap, candle, and margarine industries.

Early efforts to effect hydrogenation of oils are almost legion, and all of them were failures technically. The early work of Chevreul and Berthelot is classic, many possible methods of introducing hydrogen being attempted. Chlorine[1] bromine and iodine[2] have all been proposed. Nascent hydrogen produced from finely divided zinc and water in the presence of olein under pressure was claimed by Tissier.[3] Schmidt's process of heating zinc chloride with oleic acid at 185° was tried, without success, upon a large scale. The process of Warentrapp, in which olein is fused with caustic potash with formation of palmitic acid, had an industrial application so long as the price of olein was low. The brisk advance in recent years of the price of this material has, however, destroyed the value of the process. The processes of Wilson and of Milly transformed oleic acid into oxystearic acid by the action of sulphuric acid. The losses in the process are, however, considerable and militate against its use. Hydrogen generated by electrolysis was also tried by Petersen, who electrolysed alcoholic solutions of oleic acid acidified with a mineral acid, nickel electrodes being employed. The yields obtained did not exceed 20 per cent. Aqueous fatty material acidified with sulphuric acid and electrolysed, as well as material previously sulphonated,[4] with subsequent electrolysis, have also been proposed as solutions of the problem. De Hemptinne employed the electric discharge upon a thin layer of oil in contact with hydrogen. Repeated operation thus gave yields up to 40 per cent.

Hydrogenation by catalytic action was shown by Sabatier and Senderens to be easy of accomplishment with bodies capable of vaporisation. The patent of Senderens[5] for the reduction of the vapours of nitrobenzene to aniline by hydrogen in presence of finely divided nickel is the first patent significant of the technical development which such catalytic hydrogenation would rapidly attain.

Application of the principle to liquid media was disclosed in the patent of Leprince and Sieveke[6] and in the corresponding British patent of Normann.[7] For this latter, which has been exploited in England by Messrs. Crosfield of Warrington, a fundamental character was claimed. It was decided (1913)

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[1] Zurrer, D.R.P. 62407/1891 ; Imbert, U.S.P. 901905/1908.

[2] Goldschmidt, *Sitzungsber. K. Akad. Wiss. Wien*, 1875, **72**, 366 ; de Wilde and Geychler, *Bull. Soc. chim.*, 1889, (iii), **1**, 295.

[3] F.P. 263158/1897.

[4] Waser, D.R.P. 247454/1911.

[5] F.P. 312615/1901.

[6] D.R.P. 141029/1902.

[7] B.P. 1515/1903.

in the English courts that the Normann patent could not be regarded as constituting a monopoly of processes for the hydrogenation of oils, and consequently many other patented processes are now being used for the purpose on a technical scale. The operation of the catalytic action in liquid medium has alone rendered this technical application possible, since only a small percentage of fats and oils can be vaporised without decomposition, rendering inapplicable, therefore, the well-known procedure of Sabatier and Senderens in the vapour phase.

The numerous processes proposed may broadly be classified under four distinct headings :

(1) Processes employing reduced nickel or other base metals.
(2) Processes employing the precious metals : platinum and palladium.
(3) Processes employing oxide of nickel and oxide catalysts in general.
(4) Processes employing organic salts of nickel.

Processes employing reduced nickel or other base metals.—These processes are applications to liquid media of the Sabatier–Senderens hydrogenation reaction. Nickel is known to be the best catalytic agent of the series, copper, iron, cobalt, and other metals having also been studied.

The preparation of the catalyst material is the most important matter in the attainment of efficient hydrogenation, the aim of the operation being the preparation of the metal in a finely divided condition, generally by reduction of the oxide sufficiently dispersed throughout the liquid medium, with a high degree of catalytic activity and a low sensitivity to possible poisons, resulting in a longevity of activity. The researches of Sabatier and Senderens have shown, as previously emphasised, that the temperature of reduction of the oxide by hydrogen determines largely the properties of the catalyst. The oxide should be prepared from salts free from chlorine and sulphur, which act as poisons in the case of nickel. Copper is less sensitive to poisons, but also less active catalytically. The access of air or oxygen to the catalytic material should also be prevented, as oxidation readily occurs, even if the preparation be not pyrophoric. The life of the catalyst is generally characterised by three stages: (*a*) a period of induction, during which activity increases, (*b*) a period of normal and constant activity, (*c*) a period of diminishing activity due to poisons, deposition of inert matter or change of physical state resulting finally in a material catalytically inert.

The catalyst may be employed without any supporting material, intimacy of contact and uniformity being secured by agitating the oil. A process by Kayser has been patented on this principle.[1] The early patent of Normann indicates the possibility of rendering the catalyst more active by fixing it upon a porous support such as pumice. The use of other supports has also been proposed, as, for example, wood charcoal, talc, kieselguhr, and infusorial earths generally.

The temperature at which hydrogenation is carried out is governed by the nature of the compound to be treated and the catalytic agent used. For each compound there is a well-defined range of temperature for efficient operation. With nickel, for a number of oils, the range is from 160° to 200° with a temperature of maximum saturation velocity in the neighbourhood of 180°. With copper, the temperature is 200° and upwards.

Hydrogenation with base metal catalysts is carried out technically both at atmospheric pressure and under pressures of several atmospheres, the actual procedure adopted varying with the process employed. In certain processes, the hydrogen under pressure is utilised to assist in spraying the oil in the hydrogenation chambers. In all cases, the employment of pressures above the atmospheric will assist the progress of the catalytic action. The figures of Shaw[2] on the hydrogenation of oleic acid for the same period of time under varying pressures demonstrate the effect of pressure in diminishing the iodine value, and therefore also in raising the melting point of the material.

Pressures in atmospheres.	Temperature.	Iodine No.
5	250°	77
25	250	64
50	250	52

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[1] U.S. P. 1004035/1911.

[2] *Seifen Zeit.*, 1912, **39**, 713.

Processes employing the precious metals.—The metals platinum and palladium, owing to their well-known catalytic activity, have received considerable study as agents for hydrogenation, and latterly their employment upon a technical scale, in spite of their rareness and consequent initial cost, has been successfully achieved.

The prevailing advantage in the use of rare metal catalysts would seem to lie apparently in the lower temperature of hydrogenation required. Thus, as early as 1906, Fokin had shown that, using palladium as palladium black, oleic acid could be reduced completely to stearic acid at a temperature of 80° to 90°, whereas with reduced nickel a temperature 100° higher would be required in practice. With platinum in the form of platinum black the degree of reduction was not so great, only 24 per cent. of stearic acid being formed.

The theoretical investigations of Paal and his co-workers[1] of Willstätter[2] and others have demonstrated conclusively that numerous hydrogenations can be effected in presence of finely divided platinum or of colloidal palladium as catalyst. In general, it was found necessary to stabilise the colloidal metal, and various protective colloids were employed to effect this. Paal made use of a water-soluble protective colloid, the sodium salts of protalbinic or lysalbinic acids. Skita, who in his book "Uber Katalytische Reduktionen Organischer Verbindungen,"[3] has detailed in a comprehensive manner the literature of the subject, employed an acid-stable protective colloid such as gum arabic in place of the agents used by Paal. Solutions of platinum or palladium chloride in presence of such protective agents are reduced to stable colloidal solutions of the metal by means of hydrogen in the cold. The protective colloid also has the power of preventing the precipitation of the hydroxide of the metal when sodium carbonate is added to the solutions, the metal remaining in colloidal suspension. Such colloidal suspensions have proved to be excellent hydrogen carriers for hydrogenation of both aromatic and aliphatic unsaturated compounds. For technical operation, however, such stabilised colloidal catalytic agencies have little value, and the solution of the problem of technical

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[1] *Ber.*, 1905 to 1909, **38**, **40**, **41**, **42**.

[2] *Ibid.*, 1908, **41**, 2199.

[3] F. Enke, Stuttgart, 1912.

hydrogenation by catalysts of the precious metal type was sought in another direction.

Paal and the Vereinigte Chemische Werke of Charlottenburg have obtained numerous patents claiming the use of the noble metals for technical hydrogenation. The salts of the metals are employed in a powdered state, mixed with the fats to be hydrogenated, and treated with hydrogen at a pressure of several atmospheres at temperatures preferably below 100°.

The salts employed may be the simple compounds, $PdCl_2$, $PtCl_2$, $PtCl_4$, or the chloroplatinates, such as H_2PtCl_6, K_2PtCl_6, or the copper salt. Other acid radicals, *e.g.*, the oxalate, may be substituted for chloride. They may be brought into the reaction medium either in the powdered state or in aqueous solution ; or they may be added to the mass in a suspension in oil obtained by trituration of the solid with a small quantity of the oil to be hardened. In general, to prevent the formation, during reduction, of free acid from the salts employed, a sufficient quantity of a neutralising agent, such as anhydrous sodium carbonate, is also added. The use of carriers and porous supports for the metals is also indicated. Precipitated oxides and carbonates, talc, and infusorial earths are suggested. Further, metallic powders such as magnesium or nickel may also be employed to the same end. It is important both in the employment of double salts of the platinum metals and of metallic supports, that metals should be employed which do not act anti-catalytically in the process. Thus in this connection it is to be observed that lead acts very markedly as anti-catalyst. The researches of Karl[1] have shown that hydrogenation is very slight when lead, aluminium, iron, or zinc are used as metal supports. Oxides, hydroxides, and carbonates of the first three metals have a similar anti-catalytic effect.

The use of the metallic salts is much more effective from the hydrogenation point of view than the use of corresponding amounts of the rare metals in the form of the sponge or of the metal black, both the velocity and the degree of hydrogenation being markedly improved. The time required for reduction depends upon the amount of rare metal salt used and also upon the pressure of the hydrogen. In an example

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[1] Inaugural Dissertation, Erlangen, 1911, *Ber.*, 1913, **46**, 3069.

cited by Paal in a patent specification, using 1 part of palladium as salt with 50,000 parts of castor oil, at a hydrogen pressure of 2 to 3 atmospheres and at a temperature of 80°, the completion of the reduction process, as recognised by the gas pressure remaining constant for some considerable time, could be attained in from six to eight hours.

The recovery of the catalyst after use is an operation of importance when a catalyst of considerable costliness is employed. The methods employed consist in the main of the destruction of the colloidal nature of the catalyst and the consequent precipitation thereof. This is attained by the addition of an electrolyte such as hydrochloric acid or of aluminium chloride, which electrolytes produce an immediate flocculation. With such means, it has been found possible to hydrogenate 100 kilos. of oil, employing 1 to 2 grams of palladium, recovering from the reaction more than 90 per cent. of the catalyst.

The use of other metals of the platinum series has also been investigated. The Vereinigte Chemische Werke[1] specifies iridium, rhodium, ruthenium, and osmium as catalytic material. Lehmann[2] hydrogenated small quantities of olive oil, starting with osmium tetroxide as catalytic material, which on hydrogenation produces a colloidal solution having markedly high activity. It is obvious, however, that the capital cost of such materials will in all cases hinder their employment upon the large technical scale.

Processes employing oxide of nickel and oxide catalysts in general.—Different fundamentally from the processes detailed in the two previous sub-sections are a series of technical hydrogenation processes employing oxides as catalysts. The work of Sabatier has shown that, in general, the *rôle* of oxides in such catalytic operations is to bring about disruption of the molecule. Nevertheless, the Russian chemist, Ipatiev, as early as 1906 employed oxide of copper and nickel as catalytic agencies for hydrogenation, operating, however, at elevated temperatures (250°) and at considerable pressures (100 atmospheres).

The application of oxide catalysts to the technical hydrogenation of fats and oils is, however, in great measure due

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[1] F.P. 425729/1911.

[2] *Seifen Zeit.*, 1913, **40**, 418.

to the researches of Bedford and of Erdmann. These authors have claimed[1] that oxides of nickel act as efficient carriers of hydrogen to oils and fats, and that they possess certain advantages in practical employment over the metallic nickel catalyst. The oxide catalyst is, it is claimed, much less sensitive to sulphur and chlorine as poisons, and in addition can be operated with hydrogen, which contains relatively large quantities of oxygen containing gases, such as carbon monoxide. This gas, which appears to be a very powerful poison in hydrogenation processes employing metallic nickel, is permissible even up to high concentrations in processes using the oxide catalyst, and seems rather to function in this latter case more as a diluent than as a poison. Consequently, on the technical scale, it is allowed to accumulate in the system up to concentrations not greater than 10 per cent., its diluent effect being then sufficiently great to justify blowing off the hydrogen. According to Bedford and Erdmann, the velocity of hydrogenation is more rapid with oxide catalysts than with the reduced metal. The temperature at which the oxide catalyst works best is conditioned by the chemical composition. It is claimed that both nickel sesquioxide and nickel monoxide are effective, but at elevated temperatures, viz., 250°. On the other hand, at the low temperature of 180° it is claimed that the most efficient hydrogenation occurs if use be made of a still lower oxide of nickel, nickel suboxide. This oxide is said to be partly formed when the higher oxides are employed, and to be suspended colloidally in the oil. The increased activity of nickel oxide catalysts after a short period of employment is attributed to the formation of a colloidal suspension of this oxide. Bedford and Erdmann further claim that the activity of nickel oxide may be increased by the addition or presence of small quantities of other oxides, such as those of aluminium, silver, zirconium, titanium, cerium, lanthanum, and magnesium.

A considerable controversy has arisen as to the nature of this suboxide of nickel. It is known that oxides of nickel, when reduced by hydrogen in absence of oil at a temperature of 190°, yield metallic nickel. It is consequently claimed by many[2] that the actual hydrogen carrier in the process of

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[1] *J. pr. Chem.*, 1913, **87**, 425.

[2] *Cf.* Meigin and Bartels, *ibid.*, 1914, **89**, 301.

hydrogenation by the Bedford and Erdmann process is really metallic nickel. This point of view is disputed by Bedford and Erdmann, who believe that reduction in the presence of oil hinders the complete reduction, the oil acting as a protecting element. Erdmann is of the opinion that the suboxide forms an additive compound with the unsaturated oil, which assists in preventing reduction. The catalyst, upon removal from hardened oil, and after being freed therefrom by benzol extraction, is a strongly magnetic, black powder. A number of analyses have shown it to possess a nickel content lying between that of the metal and nickelous oxide. It is said not to form nickel carbonyl when treated with carbon monoxide under conditions in which it would readily be obtained from the metal. Like the metal, however, it yields hydrogen with mineral acids and oxides of nitrogen with nitric acid. Its main point of difference from metallic nickel appears to lie in the fact that it does not conduct the electric current, whereas mixtures of the used catalyst with a small percentage of freshly-reduced metallic nickel show a high conductivity.

The probable chemical nature of the suboxide of nickel is suggested by a research of Sabatier and Espil.[1] They have shown that if nickel oxide be reduced in a current of hydrogen at a temperature of 220°, and if the phenomena occurring be represented on a curve, plotting time against percentage of reduction, the initial rate of reduction up to 72 per cent. was considerably more rapid than the subsequent conversion. The kink in the curve would indicate the existence of a difficultly reducible oxide having a formula Ni_4O. Sabatier and Espil proved, however, the formation of nickel carbonyl with their reduced products. Moore[2] indicates the existence of a suboxide of nickel. Erdmann attempted the preparation of Moore's oxide by electrical reduction of a solution of potassium nickel cyanide. The product obtained possessed the same properties as that of the catalyst obtained from the hardened oil, and in addition showed colloidal properties towards oil. Moreover, it proved to be a good catalyst for hydrogenation.

A brief review of the patent literature concerning oxide catalysts for hydrogenation will yield some orientation as

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[1] *Compt. rend.*, 1914, **159**, 668.

[2] *Chem. News*, 1895, **71**, 82.

regards the processes in technical operation. The British patent of Bedford,[1] with the allied German patent application of Bedford, Erdmann, and Williams[2] and the allied foreign patents, represent the basic claim as regards hydrogenation with the aid of metallic oxide catalysts in general and nickel oxide in particular. The oxides of copper and of iron may be used, but are less active than the suboxide of nickel. The gas employed could be under slight pressures and composed of hydrogen with variable quantities of oxygen. A later patent[3] granted to Bedford and Erdmann relates to the production of oxides in a voluminous form for use as catalysts. The claim is for the manufacture of oxides in such form by rapid evaporation and combustion of solutions of nickel salts, for example, the nitrate, containing also large quantities of an organic compound. This latter should be rich in carbon, as, for example, the sugars, carbohydrates, gum, etc., so that on decomposition by heat a carbonaceous mass is obtained voluminous in form, which, on completion of the combustion of the organic matter, leaves the nickel in a very bulky and porous condition. According to more recent additions to their patent specifications,[4] it would seem that the suboxide is produced by heating oxide of nickel or an organic salt of nickel mixed with oil in a current of hydrogen, utilising the catalytic mass thus obtained to produce hydrogenation. An experiment cited by Bedford and Erdmann[5] illustrates this procedure. Three grams of freshly prepared nickel oxide were added to 30 grams of cotton-seed oil and hydrogenated at 260°, the oxide dispersing throughout the oil, black in colour. The hardened oil thus obtained melted at 48°. When added to 270 c.c. of cotton-seed oil and hydrogenated at a temperature of 185°, the solidifying point of the whole material after one hour's treatment with hydrogen was found to be 45°. Boberg and the Techno-Chemical Laboratories, Ltd., London, applied for a British patent,[6] which also claims the preparation of catalysts containing one or more suboxides of nickel by reduction with hydrogen of a metallic compound such as ignited nickel carbonate. It is difficult to see what

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[1] 29612 of December, 1910.

[2] D.R.P. 62366.

[3] D.R.P. 260009/1911.

[4] *E.g.* F.P. Add. 18122/1913.

[5] *J. pr. Chem.*, 1913, **87**, 446.

[6] 4702/1912.

there is novel in such claim in view of the earlier patent of Bedford previously cited.

Processes employing organic salts of nickel.—Since the elements chlorine and sulphur have been shown to be poisons with marked inhibitive action in hydrogenation with nickel catalysts, it follows that the use of the common inorganic salts of nickel, the sulphate and chloride, as starting points for the preparation of the catalytic mass, is attended by a considerable degree of risk. When these salts are employed, the nickel is precipitated from the solution as carbonate or hydroxide, and great care is taken to wash the precipitated material thoroughly free of all traces of sulphate or chloride. Owing to the colloidal nature of the precipitates, this is by no means readily accomplished, and on the technical scale the problem increases in difficulty. For successful production of catalytic material absolutely complete removal of the last traces is essential.

To avoid such difficulties, the use of salts of nickel containing none of these poisons is to be recommended. The organic salts of nickel have therefore been employed to a considerable degree for such purpose. As examples, the use of the formate, acetate, and lactate, of nickel carbonyl and of various fatty acid and amido-salts of nickel is indicated in the literature of the subject. The use of salts such as formate and acetate forms the basis of a series of patent claims by Wimmer and Higgins.[1] By employing the formate, for example, Higgins claims that the velocity of hydrogenation is accelerated by presence of the formic acid. This latter may be present to the extent of 1 or 2 per cent., and may even be introduced along with the hydrogen by passing the gas before entering the reaction chamber through a solution of the volatile acid. Alternatively, Wimmer and Higgins have proposed the preparation of catalysts by the reduction of such salts in a suitable protecting medium, such as the oil to be hydrogenated. After a period of time, the oily mass becomes black in colour, the mixture thus obtained being added to the main body of oil to be hydrogenated. The temperature of hydrogenation is apparently 180–200°. The nature of the catalyst thus obtained is doubtful. Commenting on these preparations, Erdmann

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[1] B.P. 18282/1912; F.P. 441097/1911 and 454501/1913.

states that the organic salts do not act themselves as catalysts. Bedford and Erdmann[1] claim that at 210° the salt is broken down, yielding the suboxide, which is the catalytic agent as in their process, whereas, at the higher temperature of 250°, metallic nickel is obtained. Incidentally, small amounts of nickel soaps result from the reaction. In order to suppress the concentration of free fatty acids resulting from such catalytic hydrogenation, Wimmer recommends the addition of drying agents to the catalytic material and proposes ignited sodium and magnesium sulphates for such purpose.

In order to promote intimacy of contact between catalyst and oil fat, the use of nickel soaps as catalytic agents has been suggested. De Kadt,[2] cites a mixture of the nickel and iron or copper soaps of fatty acids having a higher melting point than that of the hardened fat. After the catalytic operation is completed, the soap is separated by agglomeration of the particles in the quiescent liquid or by filtration of the hot oil, the soap being retained on the filter. The aim in this method of operation is clearly to promote mutual solubility of contact material and substrate in order the more effectively to carry the hydrogen to the unsaturated fat. In the use of such materials, however, Bedford and Erdmann claim that the oxide and suboxide are the active agents.

Nickel carbonyl, $Ni(CO)_4$, the volatile compound discovered by Ludwig Mond and used so extensively in the preparation of pure nickel, has likewise been suggested as starting point for the preparation of the catalyst. The claims of Shukoff[3] and of Lessing[4] may be mentioned in this connection. Nickel carbonyl is readily miscible with oil, and on heating to 200° is decomposed, depositing metallic nickel in a finely-divided and active form. Lessing proposes the simultaneous introduction of the hydrogen and carbonyl in order to cause the formation of the metallic catalyst in the immediate presence of the hydrogen. He suggests that the gases employed need not be of great purity and that large amounts (up to 25 per cent.) of carbon monoxide are permissible. Thus a hydrogen containing from 5 to 10 per cent. of carbon monoxide may be passed over reduced nickel and thence direct to the oil main-

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[1] *Loc. cit.*

[2] *E.g.* B.P. 18310/1912.

[3] D.R.P. 241823/1910.

[4] B.P. 18998/1912.

tained at a temperature of 200—240°, the unabsorbed gases being returned to the starting point for renewed passage over nickel and into the reaction mass. The amount of nickel required is said to be small, excellent results being yielded by 0·1 part of nickel per 100 parts of oil. Ellis has studied the use of nickel carbonyl and records similar results,[1] observing, however, that the greatest difficulty attending its use appears to be "the removal of finer portions of the nickel precipitate from the oil after hydrogenation—but this may be accomplished by the observance of due precaution in filtration." The catalyst may, he further observes, be repeatedly used, and its regeneration is, relatively, a simple matter.

The possibility of using a gas containing carbon monoxide is a factor of considerable interest in this process. From the theoretical point of view, the behaviour of this gas towards the various catalytic agents is a complex problem.[2] Most of the metallic catalysts are apparently poisoned by it. To the oxide catalysts as used by Bedford and Erdmann it is said to be indifferent, operating merely as a diluent. With nickel from the carbonyl, carbon monoxide may apparently be tolerated in considerable amount. To what must this variable behaviour be attributed? That remains an outstanding problem.

HYDROGENATION OF UNSATURATED COMPOUNDS (*continued*)

The acetylene linkage.—This is extraordinarily readily hydrogenated in presence of metallic catalysts. With nickel, acetylene and hydrogen in the volume ratio of 1 : 2 react so intensely that, with gas and catalyst originally cold, sufficient heat is developed to raise the temperature of the nickel to 150°. The product is a mixture of unchanged acetylene, some ethylene and saturated hydrocarbons, together with some carbon as a decomposition product. Excess of hydrogen favours ethane production. With excess acetylene, complex hydrocarbons, aliphatic, aromatic, and hydroaromatic, may be recovered from the product.

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[1] "Hydrogenation of Oils," p. 97, Constable, London.

[2] Maxted, *Trans. Farad. Soc.*, Sept. 1918.

The carbon–nitrogen linkages.—The triple linkage between carbon and nitrogen is readily hydrogenated with metallic nickel as catalyst. The nitriles yield the corresponding primary amine :

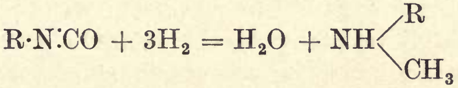
$$RC \vdots N + 2H_2 \rightarrow R\cdot CH_2\cdot NH_2.$$

Secondary reactions occur, however, in presence of such a catalyst, and so a percentage of the product is composed of secondary and tertiary amines with an accompanying formation of ammonia :

$$2R\cdot CH_2\cdot NH_2 \rightarrow (R\cdot CH_2)_2NH + NH_3$$
$$R\cdot CH_2\cdot NH_2 + (R\cdot CH_2)_2NH \rightleftarrows (R\cdot CH_2)_3N + NH_3.$$

The quadruple linkage between carbon and nitrogen present in carbylamines $R\cdot N \vdots C$, is hydrogenated at 160–180° in presence of nickel. Secondary amines of the type $R\cdot NH\cdot CH_3$ are the main product associated with small amounts of other amines.

The isocyanates, $R\cdot N{:}CO$, yield at 180–190° a secondary amine and water :

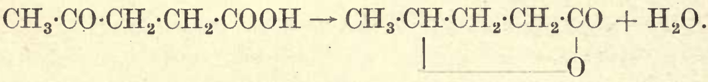


$$R\cdot N{:}CO + 3H_2 = H_2O + NH\begin{cases} R \\ CH_3 \end{cases}$$

The water formed reacts with a portion of the isocyanate, forming a disubstituted urea $(R\cdot NH)_2CO$ and carbon dioxide. The derivative of urea is in its turn hydrogenated, yielding water, and a primary and secondary amine :

$$(RHN\cdot)_2CO + 3H_2 = H_2O + NH_2R + R\cdot NH\cdot CH_3.$$

The carbon–oxygen double linkage.—Hydrogenation of the carbonyl group, CO, yields in general the corresponding secondary alcohol grouping, CH·OH. Aldehydes therefore yield the corresponding primary alcohols, with some tendency to hydrocarbon formation. Thus at 90° from formaldehyde some methane results along with the methyl alcohol ; benzaldehyde yields some benzene and toluene at 210° to 235° in presence of nickel. Aliphatic ketones yield secondary alcohols with ease by catalytic reduction and the absence of secondary reaction products is remarkable, quantitative yields being frequent. Aliphatic ketonic acids are reduced to the corresponding hydroxy-acid; subsequent elimination of water may give rise to the lactone. Thus lævulinic acid at 250° with nickel yields γ-hydroxyvaleric acid, which is immediately converted to valerolactone,



$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \rightarrow CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO + H_2O.$$

Aromatic ketones do not yield the secondary alcohol, but, on the contrary, the corresponding hydrocarbon. The quinones are readily hydrogenated to the corresponding dihydroquinones.

The benzene nucleus.—As is well known, the reduction of the benzene ring to more saturated cyclic products is, comparatively, a difficult operation by ordinary organic processes. Thus with hydriodic acid as reducing agent benzene does not yield cyclohexane, but the isomeric methylpentamethylene boiling at 69°. With the higher hydrocarbons, a certain quantity of open-chain aliphatic hydrocarbons always result. Moreover, such a procedure is not applicable at all to many of the benzene derivatives, such as phenol or aniline. Sodium amalgam and hydriodic acid have been employed with success, however, with acidic benzene derivatives.

The use of metallic catalysts has provided a method capable of fairly general application to the hydrogenation of the benzene nucleus. According to Sabatier, it is undoubtedly the most important of the operations that reduced nickel has rendered possible in synthetic organic chemistry. At temperatures in the neighbourhood of 180°, the aromatic nucleus may readily be hydrogenated in presence of nickel without isomerisation of the products or production of secondary reactions and with therefore practically quantitative yields.

Early experiments of Lunge and Akunoff[1] had demonstrated a partial hydrogenation of benzene to cyclohexane, in presence of platinum black, at the ordinary temperature, or, better, at 100°. Palladium sponge, on the other hand, yielded

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[1] *Zeitsch. anorg. Chem.*, 1900, **24**, 191.

cyclohexene, C_6H_{10}. The composition of the products was deduced from the contraction in volume of the gases, and is therefore uncertain. The catalytic activity of the metal also rapidly diminished. The work of Sabatier and Senderens demonstrated the efficiency of the reduced nickel catalyst.

Thus at temperatures above 70° benzene was directly hydrogenated to cyclohexane. The velocity of reaction attained a maximum in the temperature interval 170° to 190°, and in this range cyclohexane was produced practically quantitatively with a single passage over the catalyst, no side reactions occurring. At higher temperatures, more especially above 300°, some methane was produced and carbon was deposited in small amount on the nickel. The higher homologues could similarly be treated, yielding the corresponding homologues of cyclohexane. If, however, the substituent group were complex, as, for example, ethyl, propyl, butyl, etc., a certain quantity of a lower homologue of the saturated six-membered ring was simultaneously produced. Thus, for example, from ethyl benzene, in addition to ethyl cyclohexane, methane and methyl cyclohexane were produced, whilst from propyl benzene both methyl and ethyl cyclohexene resulted, in addition to the propyl cyclohexane. A high reaction temperature favours this dissociation of the molecule into simpler components, so that in general a temperature not higher than 180° is employed.

The reversibility of the hydrogenation processes dealt with in these pages is most apparent in connection with the hydrogenation of the aromatic nucleus. Elevation of temperature favours the reverse reaction, so that, as the temperature is raised, the yield of hydrocarbons of the cyclohexane series diminishes. At temperatures above 300°, the hydrogenation of the unsaturated bodies practically ceases, the reverse reaction completely predominating. Elsewhere in this book the dehydrogenation processes receive a general treatment, so that further comment is not necessary in this place beyond the statement that a study of the equilibria in such systems offers a profitable field of investigation for the physical chemist interested in the application of physicochemical measurement to synthetic organic processes.

Substituted benzenes with unsaturated linkages in the side chains are, naturally, converted by catalytic hydrogenation into the corresponding fully saturated hydrocarbons of the cyclohexane series. Thus phenyl acetylene, $C_6H_5{\cdot}C{\vdots}CH$, yields practically exclusively ethyl cyclohexane.

Hydrocarbons containing several aromatic nuclei are transformed into the corresponding fully saturated compounds. Thus diphenyl methane, $CH_2(C_6H_5)_2$, yields dicyclohexyl methane, $CH_2(C_6H_{11})_2$. Diphenyl, $C_6H_5{\cdot}C_6H_5$, yielded to Eykman[1] the compound $C_6H_5{\cdot}C_6H_{11}$, phenyl cyclohexane. Sabatier and Murat[2] obtained the saturated product, $C_6H_{11}{\cdot}C_6H_{11}$.

Catalytic hydrogenation of the phenols, using nickel, occurs readily in the temperature interval 180–220°. The corresponding hydroxy-derivatives of the cyclohexanes are obtained. Thus phenol yields cyclohexanol with small quantities of cyclohexanone. The operation is, however, more difficult with polyphenols, since the temperature limits in which the reaction can be effected are narrow. If the temperature is too low, reaction velocity is small, whilst at more elevated temperatures decomposition of the molecule occurs with production of phenol and benzene, which then hydrogenate normally. Derivatives of phenol such as anisol, $C_6H_5O{\cdot}CH_3$, may be hydrogenated below 150°.

Aromatic alcohols are not susceptible to catalytic hydrogenation without rupture of the molecule. Thus, benzyl alcohol yields toluene and methyl cyclohexane in presence of nickel at 150°.

Aromatic amines, as, for example, aniline, $C_6H_5{\cdot}NH_2$, yield the cyclohexyl amine with simultaneous formation of some ammonia, benzene, and cyclohexane, in addition to the formation of some derivatives of the secondary amine, $(C_6H_{11})_2NH$. Secondary alkyl aryl amines are readily hydrogenated in the aromatic nucleus at 160–180°; thus methyl aniline yields methyl cyclohexylamine.

With aromatic acids the catalytic activity of the nickel ceases after a very brief interval, as was shown by Sabatier and Murat.[3] By hydrogenation of the esters, however, with subsequent saponification, these authors obtained an 80 per cent. yield of the hexahydro-acid.

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[1] *Chem. Weekblad*, 1903, **1**, 7.

[2] *Compt. rend.*, 1912, **154**, 1390.

[3] *Ibid.*, 923.

Miscellaneous ring structures.—The hydrogenation of ring structures, other than the aromatic ring, follows the same general principles as are outlined above for the benzene derivatives. The stability of the saturated ring, however, determines whether the end product is ring or open chain. Thus, both cyclopropane and trimethylene yield propane. Cyclobutene gives first cyclobutane and then by further hydrogenation yields butane. Cyclopentadiene yields cyclopentane. Cyclohexene and cyclohexadiene both yield cyclohexane.

Tetravalent terpenes fix two molecules of hydrogen. The divalent terpenes fix one molecule. Thus limonene, menthene, and cymene all yield menthane.

Naphthalene yields tetrahydronaphthalene with nickel at 200°. At 175°, the hydrogenation may proceed further to decahydronaphthalene or naphthane. Similarly, the naphthols yield the corresponding decahydronaphthols. With anthracene, likewise, the hydrogenation is the more complete the lower the temperature at which the reaction is conducted.

Heterocyclic compounds may be reduced in presence of nickel. Pyrrol gives a 25 per cent. yield of pyrrolidine. Pyridine is only slowly reduced, but yields open-chain compounds and not piperidine. Quinoline gives an excellent yield of tetrahydroquinoline.

HYDROGENATION WITH RUPTURE OF THE MOLECULE

As exemplified in several instances cited in the previous sections, hydrogenation in presence of metallic catalysts results in a rupture of the molecule in addition to hydrogenation of the molecule and of the products of the rupture. Thus there is a general tendency for long-chain hydrocarbons to break down into simpler molecules during the hydrogenation process. Similar behaviour was noted with the substituted benzene hydrocarbons. The production of hydrocarbons other than ethane in the hydrogenation of acetylene is to be attributed to the same cause, the setting at liberty of the two CH radicals leading to combinations of various forms. Sabatier and Senderens, by treating acetylene with hydrogen in presence of nickel, obtained as much as 20 c.c. of a clear yellow liquid quite comparable with natural petroleum, possessed even of a slight phosphorescence as is usual with the natural product, and in which higher saturated hydrocarbons, such as pentane, hexane, heptane, octane, nonane, decane, etc., were all present. By suitable modifications of the *modus operandi*, yields of liquid could be obtained with properties corresponding in different samples with the various petroleums from different oil-bearing districts. The different types of oils were produced with such success that Sabatier suggested the theory that many such natural oils had been formed in such manner by catalytic action of metals on mixtures of gases in the earth's interior. This work forms an important contribution to the subject of the origin of petroleum oils.[1]

The anhydrides of fatty monobasic acids rupture when hydrogenated at 180° and yield an acid and an aldehyde,

$$(R{\cdot}CO)_2O + H_2 \rightarrow R{\cdot}COOH + R{\cdot}CHO.$$

The latter is, naturally, partially reduced to the corresponding alcohol in the process.

Hydrogenation of ethers is difficult catalytically, but when conducted above 250° rupture occurs, yielding the hydrocarbon and alcohol corresponding, the latter itself being further ruptured in part, *e.g.*:

$$(C_2H_5)_2O + H_2 \rightarrow C_2H_6 + CH_3{\cdot}CH_2{\cdot}OH$$
$$CH_3{\cdot}CH_2{\cdot}OH = CH_3{\cdot}CHO + H_2 = CH_4 + CO + H_2.$$

The action in the case of alkoxy-derivatives of benzene has already been cited. Below 150°, they hydrogenate normally in the nucleus. A certain amount of rupture simultaneously occurs, yielding cyclohexane and the aliphatic alcohol. Above 300°, however, no hydrogenation of the nucleus occurs, and the products are phenol and the aliphatic hydrocarbon or benzene and the aliphatic alcohol:

$$C_6H_5{\cdot}OR + H_2 \rightarrow C_6H_5{\cdot}OH + RH$$
$$C_6H_5OR + H_2 \rightarrow C_6H_6 + ROH.$$

Numerous examples of rupture of nitrogen-containing compounds have already been cited.

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[1] Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173; 1900, **131**, 187, 267; 1902, **134**, 1185.

CHAPTER VI

DEHYDROGENATION

CATALYTIC methods of eliminating hydrogen from organic compounds have become important in two branches of industrial chemistry, viz., the preparation of aldehydes from alcohols according to the equations :

$$C_nH_{2n+1}\cdot CH_2\cdot OH \rightleftarrows C_nH_{2n+1}CHO + H_2$$
$$C_6H_5\cdot C_nH_{2n}\cdot CH_2\cdot OH \rightleftarrows C_6H_5\cdot C_nH_{2n}\cdot CHO + H_2,$$

and the cracking of hydrocarbons into fractions of lower boiling point, *e.g.*, paraffins into petrols, ligroin, benzene, and other aromatic polycyclic hydrocarbons.

Processes of catalytic hydrogenation are usually reversible, indeed, in all cases where the products remain in the same phase during hydrogenation or dehydrogenation.

Thus benzene can be converted into cyclohexane by hydrogenation over reduced nickel at 70° to 200°. At 270° to 280° cyclohexane undergoes dehydrogenation to benzene in presence of the same catalyst.

We may thus consider the reaction :

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$$

as strictly reversible.

In this and in many other cases the process of hydrogenation proceeds most rapidly at low temperatures, the equilibrium amount of the unsaturated compound being negligible at the usual temperatures of operation.

With elevation of the temperature, all the components of the system are usually present in sufficiently large amounts to be capable of measurement, and it is practically certain that in the hydrogenation of benzene below 270° the equilibrium constant

$$K = \frac{[C_6H_6][H_2]^3}{[C_6H_{12}]}$$

could be arrived at from either side.

Unfortunately, at the somewhat elevated temperatures necessary for dehydrogenation, the unsaturated product is liable to further decomposition; thus cyclohexane always yields a varying amount of methane when undergoing catalytic dehydrogenation:

$$3C_6H_{12} \rightarrow 2C_6H_6 + 6CH_4,$$

whilst methane resulting from the hydrogenation of carbon monoxide at 180° to 200° in the presence of reduced nickel commences to undergo dehydrogenation with the deposition of carbon at 350° to 390°:

$$CH_4 \rightarrow C + 2H_2.$$

Owing to the low vapour pressure of carbon at these temperatures, rehydrogenation of the deposited carbon does not proceed on lowering the temperature to 200°, and practically complete removal of the methane may be effected.

THE PREPARATION OF ALDEHYDES FROM ALCOHOLS

We have already noted that in the preparation of formaldehyde from methyl alcohol the initial stage of the reaction is a process of dehydrogenation:

$$CH_3{\cdot}OH \rightleftarrows H{\cdot}CHO + H_2,$$

but owing to the fact that all catalysts hitherto employed to bring about this reaction gradually lose their activity for some cause with no satisfactory explanation as yet, the preparation of formaldehyde has been transformed into a fractional combustion process. The higher alcohols of the aliphatic series as well as aromatic alcohols can likewise undergo conversion into aldehydes with elimination of hydrogen in the presence of catalysts, and as such catalytic materials do not appear to lose their activity appreciably even with prolonged running, the technical development of such processes has been possible.

The dehydrogenation of primary alcohols is a reversible action :

$$R{\cdot}CH_2{\cdot}OH \rightleftarrows R{\cdot}CHO + H_2.$$

Hydrogenation of the aldehyde in the presence of reduced nickel proceeds rapidly at 180° in the case of the aliphatic compounds and below 230° for aromatic aldehydes.

As in the other cases of dehydrogenation already alluded to, no data appear to be forthcoming on the values of K, the equilibrium constant

$$\frac{C\text{ (aldehyde)} \times C\text{ (hydrogen)}}{C\text{ (alcohol)}}$$

at different temperatures for any alcohol. Elevation of the temperature, however, shifts the equilibrium over from left to right (it may be noted that the process of dehydrogenation of alcohols is an endothermic process).

At high temperatures, however, two other important side reactions proceed with measurable velocity tending to lower the yield of alcohol :

(*a*) The formation of saturated hydrocarbons by elimination of CO :

$$R{\cdot}CHO \rightleftarrows RH + CO.$$

Below 300° only small amounts of hydrocarbon are obtained with the aliphatic aldehydes, but the loss due to this reaction is usually somewhat higher in the aromatic series.

(*b*) Dehydration of the alcohol with the formation of unsaturated hydrocarbons :

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}OH \rightleftarrows R{\cdot}CH{:}CH_2 + H_2O,$$

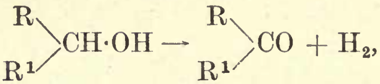
a reaction which proceeds fairly rapidly at 400° in the presence of catalysts.

The employment of metallic catalysts in the preparation of aldehydes.—In the conversion of ethyl alcohol to acetaldehyde, metallic copper, consisting usually of turnings submitted to alternate oxidation and reduction at a temperature below 250°, gives the most satisfactory results. Formation of aldehyde can already be observed at 200°, but the optimum temperature for operation lies in the neighbourhood of 310° with a permissible latitude of some 20°. At 420°, more than 16 per cent. of the acetaldehyde is converted into hydrocarbons. With relatively low space velocities (ca. 200) a 20 per cent. conversion can be effected at normal temperatures of operation. The resulting mixture of aldehyde and alcohol vapour mixed with hydrogen and a very small quantity of aldehyde condensation products are passed to a relatively large copper fractionating column, whence the alcohol can be recovered and returned to the preheater situate in front of the catalyst tubes. The aldehyde and hydrogen recovered from the middle section and top of the dephlegmating column respectively are practically pure. It is said that the conversion of alcohol into aldehyde by this means is attended with a loss of well below 10 per cent. when the due precautions are taken as regards temperature control.

Propyl, butyl, isobutyl, and isoamyl alcohol undergo similar processes of dehydrogenation with formation of the respective aldehydes at temperatures varying between 220° and 300° in the presence of metallic copper. Bouveault[1] cites the dehydrogenation of decyl alcohol, $C_{10}H_{21}\cdot OH$ under reduced pressure by similar means.

The investigation of this reaction has been extended by Sabatier[2] and by Bouveault[3] to secondary alcohols of the aliphatic series as well as to a certain number of aromatic aliphatic derivatives.

Owing to the fact that the ketones prepared by the dehydrogenation of the secondary alcohols according to the general reaction :



$$\begin{matrix}R\\R^1\end{matrix}\!\!>\!CH\cdot OH \rightarrow \begin{matrix}R\\R^1\end{matrix}\!\!>\!CO + H_2,$$

are more stable than the corresponding aldehydes,

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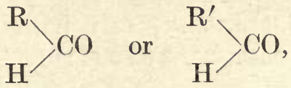
[1] *Bull. Soc. chim.*, 1908, 4, 3, 50, 119. [2] *Ann. Chim. Phys.*, 1905, 8, 4, 467.
[3] *Bull. Soc. chim*., 1906, 3, 35, 650.



$$\left.\begin{matrix}R\\H\end{matrix}\right>CO \quad \text{or} \quad \left.\begin{matrix}R'\\H\end{matrix}\right>CO,$$

temperatures higher than 300° can usually be adopted, resulting in a more effective conversion of alcohol into ketone by one passage over the copper catalyst. Sabatier states that temperatures up to 400° can be employed with safety and that a conversion of more than 75 per cent. can be effected by this means.

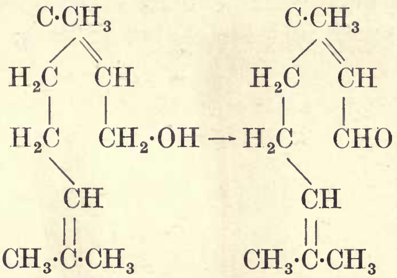
Dehydrogenation of isopropyl alcohol commences at 150°, whilst below 300° the loss due to the formation of propylene is negligible. 2-Butyl and 2-octyl alcohol are comparatively easily dehydrogenated at 300°, whilst the formation of the unsaturated hydrocarbons does not commence to be appreciable until 400°.

Aliphatic alcohols containing a double bond, *e.g.*, allyl alcohol, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, are usually converted into the saturated aldehydes :

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH \rightarrow CH_3{\cdot}CH_2{\cdot}CHO,$$

a simultaneous process of dehydrogenation and hydrogenation.

According to Bouveault,[1] geraniol is an exception, since citral is practically the only product produced by passage over reduced copper at 200° under reduced pressure :



Geraniol. Citral.

The absence of cymene in the citral, which can be easily formed by the elimination of water and closure of the ring, is under these conditions of dehydrogenation somewhat un-

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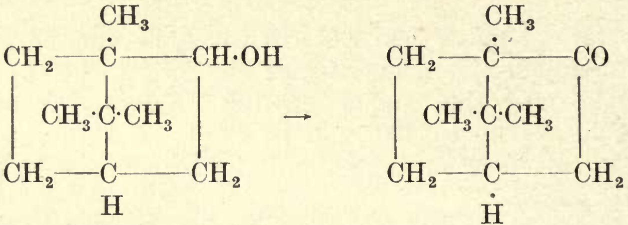
[1] *Loc. cit.*

expected. Borneol, likewise, can be converted practically quantitatively into camphor at 300° :[1]



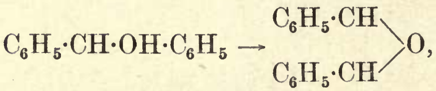
Borneol. Camphor.

In the presence of metallic copper, benzyl alcohol undergoes partial dehydrogenation at 300°, but at 380° a poor yield of benzaldehyde is obtained, degradation to toluene and benzene taking place simultaneously.

The conversion of phenyl ethyl alcohol, on the other hand, into the corresponding aldehyde is easily effected under reduced pressure.

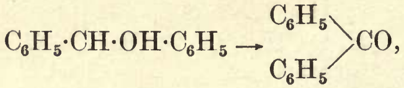
Sabatier and Senderens[2] have investigated the dehydrogenation of the alcoholic derivatives of cyclohexane. With cyclohexanol itself, the cyclohexane produced at 300° undergoes but little secondary decomposition, but with the various methyl cyclohexanols by-products such as the unsaturated ring compounds and cresols increase in amount with elevation of the temperature.

Knoevenagel and Heckel[3] record an interesting case of ether formation with metallic copper at 280° :



$$C_6H_5\cdot CH\cdot OH\cdot C_6H_5 \rightarrow \left.\begin{matrix}C_6H_5\cdot CH\\ C_6H_5\cdot CH\end{matrix}\right\rangle O,$$

whilst the conversion into benzophenone :



$$C_6H_5\cdot CH\cdot OH\cdot C_6H_5 \rightarrow \left.\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\right\rangle CO,$$

occurs when heated in the absence of copper to 280° to 295°. Sabatier cites this example as the only exception to the processes of dehydrogenation catalytically accelerated by the

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[1] Goldsmith, B.P. 17573/1906.

[2] *Ann. Chim. Phys.*, 1905, **8**, 4, 467.

[3] *Ber.*, 1903, **36**, 2816.

presence of reduced copper. It is interesting to note that these observers found that the preparation of benzophenone by this process of dehydrogenation could easily be effected in the presence of palladium black. Nickel is even more active than copper as a dehydrogenation catalyst. Thus, ethyl and the other aliphatic alcohols already undergo appreciable conversion some 50° below that found necessary in the presence of copper. Degradation of the aldehyde or ketone produced is, however, as a rule, much more marked, thus limiting the utility of this metal. For example, 75 per cent. of the propyl aldehyde produced by the dehydrogenation of propyl alcohol at 260° is destroyed during its passage over the catalyst material.

Sabatier and Senderens[1] state that reduced cobalt is intermediary between the last two elements in catalytic activity, whilst platinum and palladium exert an activity similar to that of nickel, although secondary degradation does not proceed to such a great extent. Thus in the dehydrogenation of ethyl alcohol in the presence of platinum black, although conversion commences at 270° the rapidity of conversion is not marked until a temperature of 370° is reached, when a 75 per cent. loss of acetaldehyde is obtained as a result of secondary degradations into methane and carbon :

$$C_2H_5{\cdot}OH \rightarrow CH_3{\cdot}CHO + H_2$$
$$CH_3{\cdot}CHO \rightarrow CH_4 + CO.$$

Experiments with both zinc and brass have given unsatisfactory results.[2]

The use of metallic oxides.—In the preparation of formaldehyde from methyl alcohol we have already noted that the use of certain oxides, notably those of aluminium and manganese, as catalytic materials has been attended with definite although somewhat poor yields of the aldehyde.

The extension of the use of certain oxides to the dehydrogenation of the higher alcohols has been made by Sabatier and Mailhe,[3] who arrived at the conclusion that they were less satisfactory than the metals owing to their lower reactivity, thus necessitating the use of higher temperatures with a

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[1] *Ann. Chim. Phys.*, 1905, (viii), **4**, 473.

[2] Ipatiev, *Ber.*, 1901, **34**, 3579, and 1904, **37**, 2961.

[3] *Ann. Chim. Phys.*, 1910, (viii), **20**, 313.

resulting increase in the secondary formation of hydrocarbons and carbon monoxide. These investigators have classified the oxides investigated into three groups:

(*a*) Those in which the catalytic activity for processes of dehydrogenation is most marked, *e.g.*:

$$R{\cdot}CH_2{\cdot}OH \rightarrow R{\cdot}CHO + H_2.$$

These include uranium, molybdenum, zinc, and vanadium oxides.

(*b*) Those in which processes of dehydration are accelerated, *e.g.*:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}OH \rightarrow R{\cdot}CH = CH_2 + H_2O,$$

including non-calcined chromium oxide, silica, and titanium oxide.

(*c*) Those which accelerated both reactions; including the oxide of glucinum, zirconia, and calcined chromium oxide.

With manganese oxide, dehydrogenation of the aliphatic alcohols does not commence below 360°, at which temperature the conversion is only one-fortieth of that brought about by reduced copper under similar conditions and secondary decomposition is already quite marked.

Both the oxides of cadmium and tin exhibit interesting phenomena in that their reactivities at 300° are comparable to those of metals; simultaneous reduction to metal, however, occurs. The metals themselves exhibit marked catalytic activity above their melting points, but owing to the gradual growth of large drops of the liquid metal at the expense of the smaller ones on account of their smaller vapour pressure the active surface of the catalyst is slowly reduced, causing a corresponding reduction in the space time yield for a given size of converter.

THE CRACKING OF OILS

The "cracking" or resolution of hydrocarbons of high boiling point of the aromatic and more especially of the aliphatic series into simpler hydrocarbons, both saturated and unsaturated, of relatively low boiling point, is now a well-established industry. In principle, the most effective agencies for accomplishing these changes are temperature and pressure, but the influence of catalysts apart from the specific action of surface contact both on the velocity of conversion and also on the nature of the product obtained are so marked that their industrial significance is now a matter of importance. At the same time, a study of their behaviour, although not throwing much light on the nature of the catalytic processes involved, is giving valuable information as to the methods of formation of the various products in the pyrogenetic decomposition.

To Murdock (1792) must be given the credit for the observation that the effect of heat on heavy oil was to produce a gas suitable for illumination. Since that time the cracking of heavy oils has been stimulated by the following factors: (i) the relative increase in output of very heavy oils over paraffin, petrol, and natural gas owing to the increased rate of consumption of the latter; (ii) the increased demand for petrols and petrol ethers as fuels for internal combustion engines and solvents; for paraffin in the stationary power engines of small sizes and for illumination, and for aromatic hydrocarbons as raw materials in the chemical industries.

The primary decomposition of an aliphatic hydrocarbon into its simpler constituents prior to the rearrangement by synthesis of these decomposition products into open- or closed-chain hydrocarbons is the explanation of the "cracking" process now generally adopted. All evidence[1] points to the hypothesis that catalysts exert a considerable activity in the decomposition of the original hydrocarbon and may exert a marked influence in the secondary synthesis. Since, in general, degradation and synthesis in the reactions cannot be separated, the exact functions of the catalysts employed must be considered at present as merely speculative in character.

Two alternative theories have been advanced to interpret the mechanism of the first or disintegrating stage of the cracking process, that of Berthelot,[2] and the more recent one of Bone and Coward.[3]

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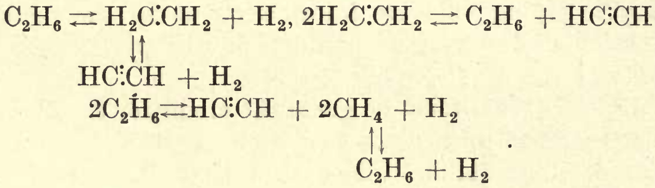
[1] See the carefully compiled literature by Lomax, Dunstan, and Thole, *J. Inst. Pet. Tech.*, 1916, **3**, 9, 36–120.

[2] *Compt. rend.*, 1866, **62**, 905; **63**, 788; and *Bull. Soc. chim.*, 1867, (ii), **7**, 251.

[3] *J. Chem. Soc.*, 1908, **93**, 1197.

According to Berthelot, disruption proceeds in stages with the primary elimination of hydrogen, with or without the simultaneous formation of methane and the production of an olefinic hydrocarbon containing one or more double bonds. Thus, ethane may be considered to undergo the following alternative or simultaneous pyrogenetic decompositions.



$$\begin{tikzcd}[column sep=small]
C_2H_6 \arrow[r, shift left] & H_2C{:}CH_2 \arrow[l, shift left] \arrow[d, shift right] & + H_2,\ 2H_2C{:}CH_2 \rightleftarrows C_2H_6 + HC{:}CH \\
 & HC{:}CH + H_2 \arrow[u, shift right] &
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
2C_2H_6 \rightleftarrows HC{:}CH + & 2CH_4 \arrow[d, shift right] & + H_2 \\
 & C_2H_6 + H_2 \arrow[u, shift right] &
\end{tikzcd}$$

The intermediary formation of olefines as well as of di- and tri-olefines during the thermal decomposition of a paraffin is a well-known phenomenon, having been confirmed by the researches of Thorpe and Young,[1] Haber,[2] and others. It is, furthermore, a matter of great technical importance in the preparation of motor spirits, since, on storage, especially under the influence of light, the di- and tri-olefines polymerise to form a gummy residue capable of making the inlet valves of internal combustion engines faulty in their action; the unpleasant smell and yellow colour of cracked spirit is also due to these compounds. Mono-olefines or chain hydrocarbons with only one double bond do not appear to possess these objectionable characters to such a high degree, and may be left in the spirit. This consideration should be noted, since the olefinic constituent of a cracked petrol is a high one, and complete removal would entail a heavy loss both in spirit and in sulphuric acid. Fractional removal of the di- and tri-olefines can be accomplished by scrubbing with 1 to 2 per cent. of sulphuric acid.

Possible hydrogenation in solution by a catalytic process or in the vapour state at a low temperature suggests itself as a promising alternative.

Bone and Coward, on the other hand, advanced the nascent radical theory On this view the hydrocarbon is considered

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[1] *Proc. Roy. Soc.*, 1871, **19**, 370.

[2] *J. f. Gasbeleucht*, 1895, **39**, 377–830; *Ber.*, 1896, **29**, 2691.

to be at least momentarily split up into radicles, $\equiv CH$, $=CH_2$, and $-CH_3$, having a fugitive existence and undergoing immediate polymerisation to more complex hydrocarbons, usually, however, simpler than the original raw material.

The formation of a double bond is an endothermic reaction, the first stage of the cracking process thus requiring the continuous supply of a considerable amount of energy, in a paraffinoid hydrocarbon amounting to approximately 30,000 cal. per gram-mol.

Rittman[1] has calculated the velocity constants of the typical cracking reaction, $C_2H_6 \rightarrow C_2H_4 + H_2$, at various temperatures with the following results :

$$K\ 500° = 0{\cdot}027$$
$$K\ 750° = 0{\cdot}074$$
$$K\ 900° = 1{\cdot}28$$

Thus, the rate of double bond formation or commencement of the cracking process is already quite appreciable at 600°.

The formation of a diolefine may be the result of the further elimination of hydrogen from a mono-olefine or, according to Ostromisslenski[2] due to thermal decomposition with the liberation of a paraffin hydrocarbon thus :

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}R \rightarrow CH_2{:}CH{\cdot}CH{:}CH_2 + RH.$$

Thus far we have shown how in the simple cracking process the production of gases, such as methane, hydrogen, the lower paraffin hydrocarbons and the olefines, can be accounted for. Such products are usually obtained in the cracking of paraffin up to 600°, whilst according to Rittman,[3] petrol formation may already be obtained at as low a temperature as 400°.

The formation of ring compounds.—According to Berthelot, the formation of acetylene is possible in the process of degradation of a paraffin under the influence of temperature and pressure with or without a dehydrogenating catalyst. Although the presence of acetylene has never actually been proved, it may be argued that almost instantaneous polymerisa-

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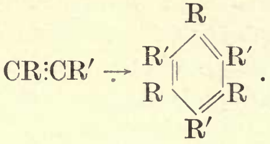
[1] *J. Ind. Eng. Chem.*, 1915, **6**, 1029 ; **7**, 945 ; 1916, **8**, 20.

[2] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 145 ; 1915, **47**, 1947.

[3] *J. Ind. Eng. Chem.*, 1915 and 1916, **7**, 1019.

tion to ring compounds takes place at the cracking temperature thus :



According to Bone and Coward, similar results would be obtained by the rapid polymerisation of the nascent radicle ⋮CH.

It must not be forgotten, however, that the formation of stable ring compounds is also possible through the condensation of olefines or dehydrogenation of a triolefine. We have already noted that the formation of polyolefines is possible in a cracking process, and our knowledge of the extraordinary reactivity of the system of conjugated double bonds—

·C:C·C:C·,

would lead us to suppose that cyclic condensation would probably proceed via a polyolefinic compound, and not through the hypothetical intermediary formation of acetylene or of the still more nascent radicle ≡CH. Ipatiev[1] has shown the formation of cyclohexane from *n*-heptane via *a* : *n*-hexylene, and Lebedev[2] the formation of the same compound from erythrene.

Cyclic polymethylenes and aromatic hydrocarbons may thus result from processes of polymerisation of olefines, diolefines and acetylenes, or by the formation of closed rings from open chains by a process of dehydrogenation.

Since, whichever view be adopted, degradation has to proceed further than in the preparation of petrols before the formation of cyclic compounds is possible, we would expect larger yields at higher cracking temperatures and especially in the presence of dehydrogenating catalysts. The optimum temperature in practice is stated by Rittman to lie between 650° and 700°; above 800°, thermal degradation to carbon and hydrogen commences to be a source of trouble and hydrocarbon loss, partly due to the ultimate dissociation of methane $CH_4 \rightleftarrows 2H_2 + C$, which is practically complete under 1 atmosphere pressure at 1200°.

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[1] *Ber.*, 1913, **46**, 1748.

[2] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249.

It must not be forgotten that, owing to the complex composition of the natural oil before cracking, the resulting product, when cracked at any given temperature and pressure of operation, will also be complex. Thus, the presence of ring compounds when petrol is desired or *vice versa*, or the occurrence of a carbon deposition in the retorts, stills, or steel tubes, can scarcely be avoided.

For the general effect of temperature and pressure on cracking processes as well as the relative advantages of cracking in the vapour or liquid state, the reader is referred to the papers by Lomax, Dunstan, and Thole cited above.

Dehydrogenation of cyclic compounds.—Sabatier and Senderens[1] showed that cyclohexane at a temperature of 270–280° in the presence of nickel underwent a process of dehydrogenation with the formation of benzene and methane :

$$3C_6H_{12} \rightarrow 2C_6H_6 + 6CH_4.$$

Substituted cyclohexanes and hydronaphthalenes behave in a similar fashion. Reduced copper is slightly less active,[2] dehydrogenation of cyclohexane commencing only at 300°.

The experiments of Cobb and his associates at Leeds University[3] on the reactions occurring among benzene and its homologues when submitted to conditions similar to those obtaining during the carbonisation of coal are of interest also from the point of view of dehydrogenation, and demonstrate the operation of such reactions in the destructive distillation of coal.

Cobb demonstrated that in a stream of nitrogen rich in benzene decomposition sets in at temperatures in the neighbourhood of 550°. A solid product, diphenyl, is one of the products of decomposition and results manifestly from a dehydrogenation process according to the reaction :

$$C_6H_6 \rightarrow C_6H_5{\cdot}C_6H_5 + H_2.$$

With increasing temperature, an increased yield of diphenyl is obtained, but, at more elevated temperatures, further decomposition sets in, a three-ring compound diphenyl benzene being produced.

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[1] *Compt. rend.*, 1897, **174**, 616.

[2] Sabatier and Mailhe, *Compt. rend.*, 1903, **137**, 240.

[3] See Wm. Young Memorial Lecture, Glasgow, Sept., 1918.

It was demonstrated that the atmosphere in which the reaction was conducted had a decisive influence on the decomposition process. Thus, with hydrogen in lieu of nitrogen as diluent, the formation of diphenyl was reduced; with a sufficient excess of hydrogen the decomposition of benzene was practically suppressed, an observation which explains the stability of benzene in the processes of coal carbonisation.

With toluene in nitrogen, similar results were obtained. At 600° the two-ring compound stilbene ($C_{14}H_{12}$) was produced. In a hydrogen atmosphere, however, hydrogenation of the molecule arose with production of methane and benzene. Xylene behaved in a similar manner.

It may be mentioned that substituted hydrogenated ring compounds behave in a similar manner. Thus piperidine was shown by Ciamician[1] to undergo dehydrogenation over nickel, between 180° and 250°, to pyridine.

Palladium black is even more active than nickel; thus, with cyclohexane, dehydrogenation commences at 170° and proceeds smoothly at 200°. At lower temperatures, viz., 100–110°, hydrogenation of benzene occurs.

Dehydrogenation of open chain hydrocarbons.—Between 350° and 400° the aliphatic saturated hydrocarbons are dehydrogenated in the presence of reduced nickel; thus pentane is finally converted into carbon and hydrogen, although the intermediary products, propane, ethane, and methane, can be isolated.

The unsaturated olefine hydrocarbons undergo similar decomposition, but part of the olefine at the same time becomes saturated. Thus in the presence of reduced nickel at 300° ethylene is converted into a mixture of ethane, methane, carbon, and hydrogen.

With cobalt, dehydrogenation commences at 300°, with iron at 350°, whilst platinum and copper exert no catalytic activity below 400°.

Acetylene, as is well known, undergoes dehydrogenation and partial polymerisation at very low temperatures. Thus, in the case of platinum black, the reactivity is already quite marked at 150°. Ferrum reductum is raised to the point of incandescence when exposed to acetylene, with the simul-

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[1] *Atti R. Accad. Lincei*, 1907, **16**, 808.

taneous production of soot. After a short period the reaction velocity becomes slower and partial polymerisation and hydrogenation of the acetylene occur.

Copper at 180° absorbs acetylene very readily, the product being a brownish-yellow modification containing a hydrocarbon cuprene, $(C_7H_6)_n$.[1] According to Sabatier, the formation of cuprene is the result of the interaction of a carbide of copper produced by the dehydrogenation of acetylene with fresh acetylene, the copper being thus decarbonised, and able, therefore, to renew its catalytic functions.

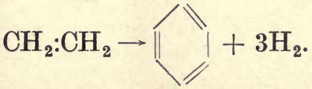
Small quantities of cuprene can also be obtained with reduced nickel in the presence of acetylene at 180°.

The formation of cyclic compounds by dehydrogenation.—This process of dehydrogenation is a very usual one in organic chemistry, and owing to the ease with which six carbon atom ring compounds are formed by loss of hydrogen from open chains, has led to the synthesis of aromatic compounds of high complexity.

Aluminium chloride is the most effective catalyst for such processes of dehydrogenation, the velocity of dehydrogenation being frequently already appreciable at 80° and vigorous at 180°. In common with other pyrogenetic reactions, simple passage through a red-hot tube will accomplish the same ends, but the yield is usually much smaller owing to the process of degradation proceeding further at such elevated temperatures. Reduced nickel is also an active catalytic material, but the necessary temperatures to be maintained are usually considerably higher than with aluminium chloride.

As typical synthesis the following may be mentioned showing the gradual formation of polycyclic compounds of high complexity.

Ethylene to benzene.



The researches of Ipatiev and Aschan[2] showed that polymerisation and dehydrogenation would proceed rapidly at 275° in the presence of aluminium or zinc chloride. Dibenzyl is

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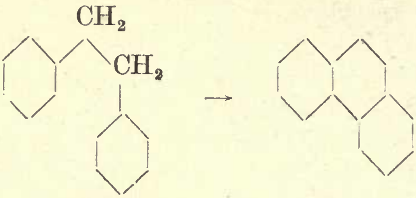
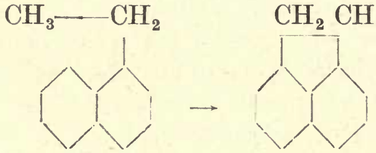
[1] Sabatier and Senderens, *Bull. Soc. chim.*, 1899, **21**, 530.

[2] *Loc. cit.*

rapidly converted into phenanthrene and *a*-ethyl naphthalene into acinaphthene by passage through a red hot tube :

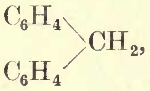


Dibenzyl Phenanthrene



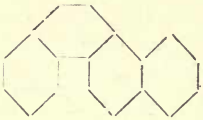
a-Ethyl naphthalene Acinaphthene

The synthesis of fluorene,

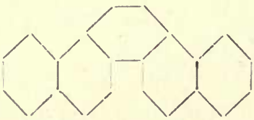


$$\begin{matrix} C_6H_4 \diagdown \\ \diagup \end{matrix} CH_2, \quad \text{i.e.} \quad (C_6H_4)_2 > CH_2,$$

chrysene,

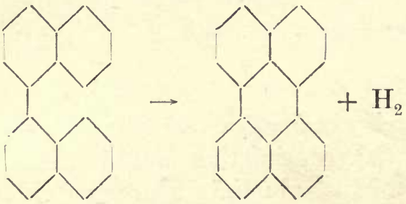


and picene,



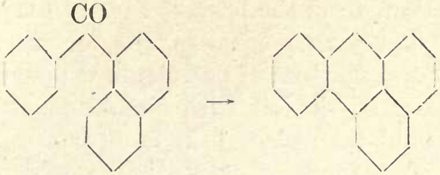
can be brought about in a similar manner.

Scholl and his co-workers[1] have paid special attention to the use of aluminium chloride in the formation of polycyclic derivatives of naphthalene and anthracene. Thus, dinaphthalene is easily converted into perylene :

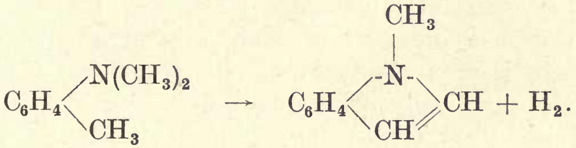


[1] *Ber.*, 1910, **43**, 1737, 2203 ; *Annalen*, 1912, **394**, 111.

In a similar manner phenyl α-ketonaphthalene can be dehydrogenated at 140° to produce benzanthrone :



Catalytic processes of dehydrogenation can also be applied to the formation of heterocyclic compounds. Carrasco and Padya[1] showed that dimethyl o-toluidine in the presence of reduced nickel at 300° was partly converted into methane, toluidine and methyltoluidine, more than 24 per cent. of methylindol being, however, simultaneously produced :



$$C_6H_4\left\langle\begin{matrix}N(CH_3)_2\\CH_3\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}\overset{CH_3}{\overset{|}{-N-}}\\CH\end{matrix}\right\rangle CH + H_2.$$

Methyl o-toluidine with similar treatment yields a small quantity (6 per cent.) of indol.

Use of metals in cracking processes.—In 1866, Berthelot noted the catalytic decomposition of acetylene to carbon and hydrogen in the presence of finely divided iron.

Moissan and Moureau[2] confirmed Berthelot's results and showed that cobalt, and especially nickel, when freshly prepared, exhibited similar marked activity.

In 1910 Ostromisslenski[3] showed that crude Russian petroleum, when passed over reduced nickel at 600–700°, was completely disintegrated to hydrogen, methane, and a carbonaceous residue. Ubbelohde,[4] working at 350°, showed that the cracking process had already commenced to produce lighter distillates at a temperature some 100° lower than would be necessary in the absence of any catalytic material.[5] Zanetti[6] conclusively showed from experiments on propane and butane that nickel

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[1] *Gazzetta*, 1907, **37**, 12149.

[2] *Compt. rend.*, 1896, **122**, 1241.

[3] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 195.

[4] *Petroleum Zeit.*, 1912, (vii), **9**, 334, 1233, 1911.

[5] See Lamplough, B.P. 19702/1912.

[6] *J. Ind. Eng. Chem.*, 1916, **8**, 674.

was an effective catalytic material in the preparation of petrols, but not for the formation of aromatic substances. These observations form the basis of several patents.[1] Several patents have likewise been taken out for the use of nickel as a catalyst, for a mixture of petroleum vapour and hydrogen, so that cracking of the oil with simultaneous saturation of the olefines would take place.[2] It is, of course, unlikely that any process of secondary saturation would occur at the elevated temperatures, 350–450°, necessary for the cracking process itself.

The experiments of Ipatiev, Engler, Kuznetzov, and others showed that copper, iron, or aluminium showed no advantages over nickel as catalytic agents. We may conclude that the use of reduced metals, especially nickel, in cracking processes is of some material advantage, when petrol is the desired product; in the presence of such a catalyst, the cracking temperature is appreciably lower, the formation of aromatic compounds practically eliminated, and the olefine content of the finished spirit may be slightly reduced by secondary hydrogenation. Technical difficulties such as the deposition of carbon on the surface of the catalyst must, however, be expected.

Use of metallic oxides in cracking processes.—Alumina[3] and titanium dioxide[4] exert a slight catalytic activity at 350°, paraffins being partly dehydrogenated at this temperature, whilst at higher temperatures the yield of aromatic compounds is sensibly increased by the presence of such catalytic oxides. Hirschberg[5] claimed an extraordinary activity for chromium oxide prepared by the ignition of ammonium bichromate.

Ipatiev was able to isolate various aromatic hydrocarbons from the residues obtained by the passage of ethylene over alumina at 380–400° under 70 atmospheres pressure. In the absence of alumina, cyclic paraffins and olefines only were obtained. Similar results were obtained by this investigator with cyclohexane at 500° under high pressures. With

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[1] Hall, B.P. 17121/1913; Higgins and Preston, B.P. 23876/1914, and others.

[2] Phillips and Buttell, B.P. 23977/1907; Planes, Ltd., B.P. 5245/1913.

[3] Ubbelohde, *loc. cit.* [4] Zelinski, *J. Russ. Phys. Chem. Soc.*, 1915, **48**, 610.

[5] B.P. 1414, 4573, 1905.

n-hexane at 650° under normal pressures no aromatic substances were obtained.

It may be concluded that the use of the oxides of aluminium, titanium, and chromium might be of slight service where a high yield of aromatic hydrocarbons is desired and the cracking process is conducted under elevated pressures.

The Friedel and Crafts reaction where the halides of certain elements, especially aluminium, are used as catalytic agents, form the basis of several patents on cracking processes. (Athel, B.P. 4764/1877; B.P. 7112/1913; B.P. 17838/1913, and especially McAfee, B.P. 22243/1914; U.S.P. 1127465/1915, also *J. Ind. Eng. Chem.*, 1915, 7, 737).

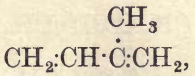
It is claimed that "heavy" petroleum is readily converted into aromatic hydrocarbons whilst the polymerisation of the olefines proceeds rapidly in the presence of the halides of aluminium and zinc.

At high temperatures, circa 1000°, methane and the simple olefines only result,[1] whilst at very low temperatures polymerisation to cyclo-paraffins occurs. Ipatiev obtained a good yield of naphthalenes at 375°, from ethylene at 70 atmospheres pressure in the presence of zinc chloride; aluminium chloride was even more active.

ISOPRENE

In view of the importance of the possible technical development of a process for producing rubbers and even terpenes such as camphor from coal tar, shale, or crude oils, it may be mentioned that the simplest hydrocarbon which offers a reasonable opportunity for an economic synthesis of these substances is hemiterpene or isoprene (methyl divinyl), C_5H_8, or one of its simple derivatives.

Isoprene contains two ethylene linkages,



$$CH_2{:}CH{\cdot}\overset{CH_3}{\dot{C}}{:}CH_2,$$

and is the usual residuum obtained in fairly large quantities on the distillation of any terpene or rubber.

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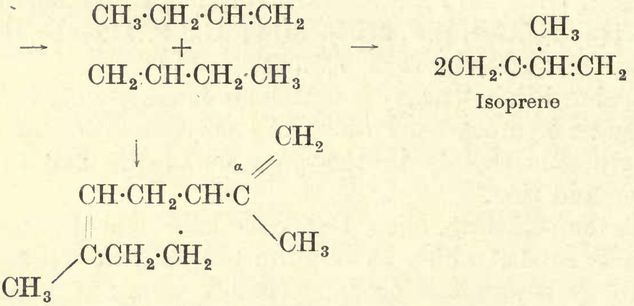
[1] Gustavson, *J. Russ. Phys. Chem. Soc.*, 1881, **13**, 1149.

Ostromisslenski[1] has already shown that dipentene and dihexene produced by dehydrogenation of pentane and hexane or the elimination of methane from hexane and heptane, with subsequent polymerisation of the olefine when heated to 500° give appreciable quantities of isoprene and dimethyl divinyl. We may thus consider that the first steps in the synthesis of isoprene are as follows :

$$\underset{\text{Hexane}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \rightarrow \underset{\text{Pentene}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2} + CH_4$$



$$\rightarrow \begin{matrix} CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \\ + \\ CH_2{:}CH{\cdot}CH_2{\cdot}CH_3 \end{matrix} \rightarrow \underset{\text{Isoprene}}{2CH_2{:}\overset{CH_3}{\dot{C}}{\cdot}CH{:}CH_2}$$

Dipentene

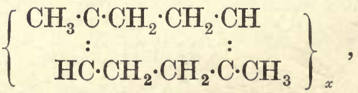
The double bonds in the a, ϵ position show their usual tendency to form a conjugated system with rupture of the molecule to take up the a, γ positions.

According to Berthelot, isoprene and similar derivatives of divinyl do not appear to result from the decomposition of a paraffin, but through the intermediate formation of a complex triolefine. Ostromisslenski postulated the formation of a simple olefine which would then break down at 500° to form divinyl :

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}R \rightarrow CH_2{:}CH{\cdot}CH{:}CH_2 + RH.$$

Isoprene on condensation forms a polymer having a rubber-like consistency.

Harries suggests that rubber has the following constitution :



$$\left\{ \begin{matrix} CH_3{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH \\ \vdots \qquad\qquad \vdots \\ HC{\cdot}CH_2{\cdot}CH_2{\cdot}C{\cdot}CH_3 \end{matrix} \right\}_x ,$$

a simple polymer of isoprene.

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[1] *J. Russ. Phys. Chem. Soc.*, 1905, 47, 703 *et seq.*

The catalysts employed in the polymerisation of isoprene to rubber.—Greville Williams[1] was the first to observe that a rubber-like compound could be obtained by the dry distillation of isoprene which had been allowed to stand exposed to the air. Bouchardat[2] obtained "a substance analogous to natural caoutchouc" by the action of concentrated hydrochloric acid, five times the weight of the isoprene employed, contained in sealed glass tubes for several weeks.

Three years later Tilden[3] noted that nitrosyl chloride was as effective as hydrochloric acid in accelerating the polymerisation of isoprene. The same investigator noted[4] the polymerisation through the agency of time and light, and showed that the polymerisation product possessed many of the properties of natural caoutchouc, even to the action of sulphur effecting vulcanisation.

Kondakow[5] effected the polymerisation of dimethyl 2 : 3-butadiene-1 : 3, a homologue of isoprene, to a rubber by subjecting it to the action of alcoholic potash for three days.

Lebedev,[6] utilising daylight, Ostromisslenski and Koch[7] with ultra-violet radiation, and Collie,[8] with the silent electric discharge, all effected the complete and relatively rapid conversion of isoprene into rubber, this being superior to all chemical catalysts thus far investigated, with the possible exception, perhaps, of oxygen or ozonised air, when relatively large quantities of simple polymers, usually the dimeride and trimeride, are generally obtained.

With the increase in the price of rubber subsequent to 1906, the problem of rapidly effecting the complete polymerisation of isoprene was attacked with renewed vigour. Harries in 1910 showed that heating to 90–100° in a sealed tube with acetic acid for eight days effected the conversion, but the yield of rubber was extremely variable. Hoffmann and Coutelle,[9] of the Bayer firm, made the important observation that pure

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[1] *Phil. Trans.*, 1860, **150**, 254.

[2] *Bull. Soc. chim.*, 1875, **80**, 1446; *Compt. rend.*, 1879, **89**, 361.

[3] *Chem. News*, 1882, **44**, 170.

[4] *Ibid.*, 1892, **65**, 205.

[5] *J. pr. Chem.*, 1901, **64**, 109.

[6] *J. Russ. Soc.*, 1909, **41**, 1868.

[7] *Chem. Zeitsch.*, 1912, **36**, 150.

[8] *J. Chem. Soc.*, 1905, **87**, 1540.

[9] F.P. 414382/1909.

isoprene or its isomers rapidly polymerises to caoutchouc with good yields when subjected to heat, either in the presence of or without catalytic agents. Previous attempts at thermal polymerisation were unsuccessful, doubtless due to the presence of impurities. Matthews in 1910[1] showed that metallic sodium was a polymerising catalyst of unique activity. According to Harries,[2] butadiene is converted at the ordinary temperature in a few hours; isoprene is converted at about 60° almost quantitatively into caoutchouc without the formation of any dimerides in from fifty to one hundred hours, whilst the sodium for the greater part is unaltered.

Sodium-condensed caoutchouc is, however, of different structure from that obtained by polymerisation by heat or with the aid of acetic acid, and probably has the following structure proposed by Harries:

$$\left\{ \begin{array}{l} CH_3{\cdot}C{:}CH{\cdot}CH_2{-}CH{\cdot}CH_3 \\ CH_3.\dot{C}H{\cdot}CH_2{\cdot}CH{:}\dot{C}{\cdot}CH_3 \end{array} \right\}_x$$

Various other catalytic agents have been proposed from time to time, such as acetic anhydride,[3] cerium or vanadium salts,[4] and sodamide,[5] but do not appear comparable in activity with either acetic acid or metallic sodium as condensing agents.

Mention may be made of an interesting series of catalytic reactions proposed by De Boistesselin and Dubosc,[6] in which methane and acetylene are used as raw materials. It is proposed to pass methane over carbon deposited on copper oxide at 400° to 450° when, it is stated, ethylene is obtained together with some of the higher olefines,

$$CH_4 + 3C \rightarrow 2C_2H_2.$$

Dubosc states that the proportions actually obtained were:

Ethylene	36	per cent.
Butylene	42	,,
Higher olefines and hydrogen	21	,,

If butylene and acetylene in equivalent proportions be passed

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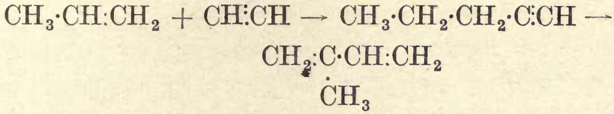
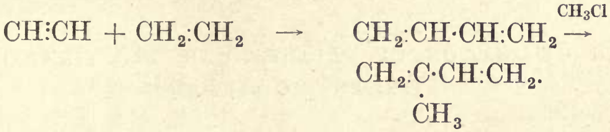
[1] F.P. 437547/1910; B.P. 24790/1910. [2] *Annalen*, 1911, **383**, 157.
[3] F.P. 433825/1910. [4] F.P. 440173/1910. [5] B.P. 9219/1910.
[6] "Rubber, Its Production, Chemistry and Synthesis," Griffin, 1918.

over animal charcoal heated to 150°, isoprene is produced according to the following reactions :



$$CH_3\cdot CH{:}CH_2 + CH{\vdots}CH \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot C{\vdots}CH \rightarrow CH_2{:}\underset{CH_3}{C}\cdot CH{:}CH_2$$

Ethylene, in a similar manner, can be converted into isoprene by interaction with acetylene followed by subsequent methylation with methyl chloride :



$$CH{\vdots}CH + CH_2{:}CH_2 \rightarrow CH_2{:}CH\cdot CH{:}CH_2 \xrightarrow{CH_3Cl} CH_2{:}\underset{CH_3}{C}\cdot CH{:}CH_2.$$

From the above short review it appears that the synthesis of many derivatives of the terpenes as well as of the rubbers from simple oils or tars, through the intermediary of divinyl and its derivatives, is by no means an insoluble problem.

CHAPTER VII

THE UTILISATION OF CATALYSTS IN THE FIXATION OF ATMOSPHERIC NITROGEN

During the last ten years several technical solutions to the so-called nitrogen problem have been put forward and developed. The tremendous increase in the demand for nitric acid and nitro-explosives necessitated by the world-war has stimulated research and attracted public attention in a manner which, unfortunately for England, Sir William Crookes's presidential address to the British Association in 1898[1] failed to do. It is to be hoped that in the near future our economic safety, which is chiefly dependent on agriculture, will be assured by the erection of suitable plant either under national control or through the enterprise and initiative of English manufacturers.

The various processes which have been developed for the fixation of nitrogen may be chiefly enumerated as follows:

(1) The arc process for the oxidation of atmospheric nitrogen.
(2) The preparation of ammonia by the direct combination of hydrogen and nitrogen.
(3) The cyanamide and nitride processes.
(4) Various cyanide processes.

In addition, it must be recorded that the direct fixation of nitrogen with the aid of certain bacteria has been successfully accomplished, although no economic system has as yet been developed.

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[1] "The Wheat Problem," 3rd edn., 1917.

THE ARC PROCESS

The preparation of nitric acid and nitrates from the nitric oxide produced in the passage of air through an electric arc has been developed on a very large scale in Scandinavia, where the relative cheapness of electric power goes far to compensate for the electrical inefficiency of the process.

The primary formation of nitric oxide from its elements proceeds according to the following reaction :

$$O_2 + N_2 \rightleftarrows 2NO$$

The synthesis and decomposition of nitric oxide from its elements was first shown by Cavendish and Priestley, whilst the more exact equilibrium concentrations at various temperatures were investigated by Nernst and Jellinek.[1] The appended table indicates the close agreement obtained by these investigators between the observed figures and those calculated.

The formation of nitric oxide is endothermic at the ordinary temperature, being accompanied by the absorption of 43,200 cal. per 2 gram-mols. of nitric oxide formed.

The variation of the equilibrium constant

$$K = \frac{[NO]^2}{[N_2][O_2]}$$

with the temperature is accordingly found by the van't Hoff equation :

$$\frac{d \log K}{dT} = \frac{43,200}{RT^2}$$

Absolute temperature.	NO observed, per cent.	NO calculated, per cent.
1811°	0·37	0·35
1877	0·42	0·43
2033	0·64	0·67
2580	2·05	2·02
2675	2·23	2·35

Obviously, therefore, increase in temperature of synthesis favours increased yield of nitric oxide.

The general description of the various arc process plants

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[1] *Zeitsch. anorg. Chem.*, 1906, **49**, 213 ; 1906, **49**, 229.

now in operation, of which the most important is undoubtedly the Birkeland-Eyde magnetically spread arc, followed by the Schönherr extended arc and the Pauling make and break arc processes, is somewhat beyond the province of this volume. It may be pointed out, however, that only from 70 to 75 grams of nitric acid are obtainable per kw. hr. from even large installations, indicating an electrochemical efficiency of only some 3 per cent.

During the last few years attention has been paid to the possibility of increasing the yield of nitric acid obtainable from this source, as a result of which two points in which catalytic operations appear to be involved may be noted.

In the technical operation of the various arc processes the average concentration of nitric oxide in the eflowing gases scarcely ever exceeds 2·5 per cent., and usually lies between the limits of 1·5 and 2·2 per cent. The mean temperature of the inner and hottest zone has been computed to be more than 3500°, equivalent to a thermal equilibrium concentration of more than 6 per cent. of nitric oxide.

Nernst and Brodie[1] have actually found these high concentrations in the gas of the inner zone by analysis of samples withdrawn through a platinum capillary. These investigators pointed out that the low concentrations technically obtained were caused by the continuous alteration of the equilibrium concentration occurring during the cooling of the gases as they passed through the outer and cooler zones. They showed that the velocity with which the decomposition of the nitric oxide proceeds according to the equation :

$$-\frac{dx}{dt} = k_1[\mathrm{NO}] - k_2[\mathrm{N_2}][\mathrm{O_2}],$$

was extremely rapid above 1300°, and consequently the large quantities present in the inner zones were largely decomposed before they could be cooled to below this temperature, at which the velocity of decomposition becomes negligibly slow, the necessary conditions thus obtaining for a "frozen" equilibrium.

Recent experiments of Rossi have indicated that another factor may play a prominent part in the catalytic decomposition

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[1] *Zeitsch. Elektrochem.*, 1905, **11**, 752.

of the nitric oxide during its passage from the hot inner zones to the metastable cooler zones of artificial equilibrium below 1300°. It seems probable that the electrode dust produced in the mechanical pulverisation by the electric discharge may exhibit a very marked catalytic activity.

In the Birkeland-Eyde furnace water-cooled copper electrodes are employed, whilst the Schönherr and Pauling furnaces employ iron electrodes. Rossi has indicated that both copper and iron oxides appear to hasten the decomposition of nitric oxide, whilst lead and aluminium oxides are catalytically inert. In a small furnace of the Pauling type increased yields were obtained when composite lead aluminium electrodes were substituted for the usual iron kindling blades.

The second point of interest centres round the work of Haber and Koenig[1] conducted on water cooled arcs operated under reduced pressure where the maximum temperature probably did not exceed 1800°. No precautions were taken to "freeze" the equilibrium. Under these conditions, nearly 10 per cent. of nitric oxide was obtained, a figure entirely incompatible with the observations of Nernst and Jellinek. It must be assumed either that in the extrapolation from Nernst and Jellinek's figures up to high temperatures serious errors have been introduced, and that a certain amount of decomposition had already occurred even with the precautions taken by Nernst; or, as seems more likely, the combination of nitrogen and oxygen can be brought about by electrical means. Reference may be made to the work of Lowry,[2] Fischer and Hene[3] and Strutt,[4] on the activation of atmospheric nitrogen and oxygen. It is evident that sufficient thermal energy is available to produce these relatively high concentrations of nitric oxide, and the ionisation of the gas by electrical means may be regarded as a catalytic operation, although, as has been noted above, the equilibrium concentration arrived at differs from that obtainable by purely thermal methods.

In all arc processes the resulting nitric oxide-containing gas is rapidly cooled to below 1100° and thence more slowly to

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[1] *Zeitsch. Elektrochem.*, 1907, **13**, 725; 1908, **14**, 689.

[2] *Trans. Farad. Soc.*, 1913, **9**, 187.

[3] *Ber.*, 1913, **46**, 603.

[4] *Proc. Roy. Soc.*, 1911, **85**, 219, 577 *et seq.*

40°, the sensible heat in the gases being usually utilised to raise steam.

At 620° the nitric oxide commences to combine with oxygen to form nitrogen dioxide :

$$2NO + O_2 \rightleftharpoons 2NO_2,$$

and is nearly complete at 140°. For the mechanism of absorption of nitrogen dioxide in water the investigations of Le Blanc,[1] Foerster and Koch,[2] Lunge and Berl,[3] and others may be consulted.

It appears from a study of the literature, and from experience in the operation of nitric acid towers, that the reactions involved are relatively complicated, and the velocity coefficients of certain of these are so slow as to render their technical operation a matter of some difficulty. The slowness of absorption in the formation of nitric acid is probably chiefly due to the slow reaction velocity of the above reaction and the need of some catalytic agency is clearly indicated. The use of small quantities of chlorine or bromine vapour has been suggested as efficient catalysts, but the difficulties incurred in elimination of the chlorine or bromine from the resulting nitric acid has been the chief objection to their extended use.

THE PRODUCTION OF SYNTHETIC AMMONIA BY THE HABER PROCESS

The technical production of pure ammonia by the catalytic combination of nitrogen and hydrogen must be considered as one of the greatest triumphs of modern physical and engineering chemistry.

In 1865, Deville[4] observed that the decomposition of ammonia under the influence of a spark discharge was never complete, thus indicating the reversibility of the reaction :

$$2NH_3 \rightleftharpoons N_2 + 3H_2.$$

The recent communication of Prof. C. Matignon to the

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[1] *Zeitsch. Elektrochem.*, 1906, **12**, 541.

[2] *Zeitsch. angew. Chem.*, 1908, **21**, 2161.

[3] *Ibid.*, 1906, **19**, 807.

[4] *Compt. rend.*, 1865, **60**, 317.

inaugural session of the "Société de Chimie Industrielle" presents a very great interest to all concerned in ammonia synthesis in particular and also in the application of science to industry in general. The communication records a research into the scientific literature and more especially the patent literature concerning the production of ammonia from its elements.

A *résumé* of the patents as set forth by M. Matignon may be given. Dufresne, in 1865, took out a British patent,[1] in the name of Charles Tellier for the preparation of oxygen. In the patent it is stated that "a large quantity of nitrogen is liberated in these operations. To utilise this gas, I pass it over spongy iron heated to redness and which absorbs nitrogen. In this state I then pass hydrogen over the combination of iron and nitrogen thus formed. Decomposition is immediate and the great quantity of ammonia thus produced lowers the price of oxygen."

Tessie du Motay[2] took out a patent for a continuous process of ammonia synthesis. The production of ammonia was to be effected by passage of hydrogen and nitrogen alternately over tubes containing the nitrides of titanium heated to redness. The nitrides Ti_3N_2 and TiN, heated with hydrogen, yield ammonia and the nitride Ti_5N_3, which is reconverted by nitrogen to TiN and Ti_3N_2.

Charles Tellier[3] proposed to unite nitrogen and hydrogen by alternate passage over heated iron. Spongy iron is recommended, the two gases to be obtained by the respective actions of steam and air on zinc.

The patents of the Société Azote de Paris represented by Charles Tellier[4] embodies the following claims: (1) The preparation of nitrogen and hydrogen by the respective action of air and steam upon zinc. (2) The alternate passage of nitrogen and hydrogen through heated vessels filled with spongy titaniferous iron to produce ammonia. (3) The employment of pressure up to 10 atmospheres, using heated vessels containing platinum deposited on pumice or charcoal. (4) The use of titaniferous iron admixed with another metal.

[1] No. 1833.

[2] F.P. 92346/1871.

[3] F.P. 138472/1881.

[4] D.R.P. 17070/1881.

Ramsay and Young, in 1884, recorded the formation of small quantities of ammonia by passage of nitrogen and hydrogen over heated iron wires.

An Austrian patent of Hlavati[1] claimed the synthesis of ammonia by passage of hydrogen and nitrogen through a heated chamber containing as catalyst a mixture of titanium or titaniferous bodies in admixture with platinum supported on porous materials.

A Norwegian company, Christiania Minekompanie, took out the French patent No. 225183/1896 with several important claims. Nitrogen and hydrogen were to be passed through heated vessels containing titanium precipitated in a finely divided condition on neutral supports, with or without the addition to the titanium of platinum or the platinum metals; further, the titanium could be replaced by bismuth, antimony, or alkali or alkaline earth metals, but in such cases platinum and the platinum metals were to be employed.

In 1901, Le Chatelier patented[2] the direct combination of hydrogen and nitrogen in which he specially claims the use of high pressures up to 100 atmospheres in order to facilitate combination, coupled with the use of appropriate catalytic material.

Perman noted the activity of reduced iron, copper, zinc, cobalt, nickel, palladium, etc., in promoting the combination of nitrogen and hydrogen, and showed also the advantage of pressure.

In 1904, the subject was again taken up by Haber and his co-workers, especially Van Oordt and Le Rossignol[3] and was carried to the stage of a complete technical success by the Badische Anilin- & Soda-Fabrik at Oppau.

Haber first investigated the equilibrium conditions obtaining between a mixture of nitrogen, hydrogen and ammonia at varying temperatures. Equilibrium was obtained by the passage of nitrogen and hydrogen over various catalytic materials and was also arrived at from the other side by the decomposition of ammonia. As catalytic materials, iron,

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[1] Austr. P. 45/2938, 1895.

[2] F.P. 313950/1901.

[3] *Zeitsch. anorg. Chem.*, 1905, **43**, 111; *Ber.*, 1907, **40**, 2144; *Zeitsch. Elektrochem*, **14**, 181, 513, 1908, 1910, 1913; also Eighth Int. Congress App. Chem. New York, 1912.

nickel, chromium, and manganese were used at temperatures ranging between 700° and 1000°.

The following values of the equilibrium concentration of ammonia were obtained in a gas mixture of nitrogen (1 volume) and hydrogen (3 volumes) at atmospheric pressure. The value of K, the equilibrium constant, can easily be deduced from the equation :

$$K = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$$

Temperature.	NH_3 per cent.
700°	0·0221
800	0·0109
850	0·0091
1000	0·0048

It will be noted that the equilibrium concentration of ammonia decreases with increasing temperatures,[1] the equation $N_2 + 3H_2 = 2NH_3$ being exothermic, evolving 23,780 calories per 2 gram-mols. of ammonia.

The equilibrium concentrations at relatively low temperatures were calculated by means of the formula :

$$\log_{10} K = \frac{2215}{T} - 3{\cdot}626 \log_{10} T + 3{\cdot}07\, T.10^{-4} + 2{\cdot}9\, T^2\, 10^{-7} + 4{\cdot}82.$$

Nernst and Jost,[2] by an application of the Nernst heat theorem to Haber's results, indicated that his figures were somewhat too high, and conducted a series of experiments at high pressures (viz., 70 atmospheres), when, as is indicated from the equilibrium equation, greater quantities of ammonia are formed. Haber repeated these experiments at 30 atmospheres, and it was finally shown that Nernst's figures were the more correct. On the basis of this investigation, Haber, at the request of the Badische Co. undertook the preliminary development of a technical synthesis, which was finally brought to a brilliant success by the company independently of the originator.

The exact details of the process developed by the Badische firm are carefully guarded national secrets. During the period

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[1] Recently it has been shown that the values of K pass through a minimum and increase again at very high temperatures. See Maxted, *J. Chem. Soc.* 1918, **113**, 168 and 386.

[2] *Zeitsch. Elektrochem.*, 1907, **13**, 521 ; 1908, **14**, 373 ; 1910, **16**, 94.

of the war, small experimental Haber units have been at work in all the allied countries and have gone far to confirm the statements published from time to time by the Badische Co. as to the relative merits and disadvantages of the process.

The following considerations will indicate briefly the nature of the fundamental problems involved. The cost of the preparation of the gases, and more especially of the hydrogen of a sufficiently high degree of purity, constitute more than 75 per cent. of the working costs ; and it may be stated definitely that the commercial possibilities of the synthetic process rest on the production of pure hydrogen at an economic rate. The Badische Co. developed the water-gas catalytic process for the production of their hydrogen (see Ch. V), the nitrogen being obtained by the fractional distillation of liquid air. An alternative method of producing the desired 3 : 1, $H_2 : N_2$ mixture would be obtained from a special semi-water-gas plant, in which the air-steam blows and makes were so adjusted, and the gaseous products mixed, as to give the desired mixture after the catalytic operation was completed.

It may be pointed out that this latter method, although possibly more economical than the dual process, would involve the presence of a not inconsiderable quantity of inert gas, *e.g.*, argon, neon, and the like, a point which will be referred to later.

The carbon dioxide is removed by counter-current washing with water under pressure, subsequently followed by an alkali scrubber to remove the hydrogen sulphide and the final residue of carbon dioxide, whilst the 2–3 per cent. of the carbon monoxide is nearly, but not completely, eliminated by scrubbing the gases compressed to 70 atmospheres with a 25 per cent. caustic soda solution maintained near its boiling point under pressure. Under these conditions, sodium formate is formed according to the equation :

$$\mathrm{NaOH + CO = H{\cdot}CO{\cdot}ONa.}$$

Removal of the carbon monoxide is completed by scrubbing the gas mixture with cuprous ammonium carbonate solution, the pressure being still maintained ; and the resulting nitrogen–hydrogen mixture is now free from all impurities except the inert gases and possibly traces of methane, oxygen, or carbon monoxide and water vapour. To insure the absence of oxygen and carbon monoxide, the gases may be passed over nickel maintained at relatively low temperatures, so as to form methane from any carbon monoxide and water from any oxygen present in the gases. The mixed gases are now further compressed from the 70 atmospheres at which carbon monoxide removal is accomplished to between 100 and 200 atmospheres, probably 150, at which pressure the ammonia synthesis is accomplished. During compression, most of the water vapour in the gas is removed, and the remainder is eliminated by the use of calcium chloride and possibly other desiccating agents such as metallic sodium or sodamide. The gases are now ready to pass to the catalyst furnace itself. It has been already pointed out that the equilibrium amount of ammonia obtainable at a given gas pressure is greatly increased by lowering the gas temperature, but, unfortunately, the sensitiveness of the reaction velocity to the lowering of the gas temperature is also extremely marked. Both Haber and the Badische Co. conducted several years of patient research before obtaining satisfactory catalysts active at low relative temperatures. Both osmium and uranium (including uranium carbide, the usual technical preparation) were found to be excellent catalysts, being still quite markedly active at 350°, but owing to the high cost of the former and the great sensitiveness of the latter substance even to minute traces of catalytic poisons, their technical utilisation could not be considered.

The solution of this problem appears to have been found in the use of some form of an iron catalyst. The activity of iron as a catalyst for the ammonia synthesis is greatly dependent on its method of preparation, together with the presence of certain promoters and the entire absence of certain catalyst poisons. A study of the recent patent literature on the subject reveals the fact that molybdenum, tungsten, cobalt, and uranium appear to be the most efficient promoters for the iron catalyst, whilst the presence of small quantities of alkalies appears advantageous; as poisons, sulphur, selenium, tellurium, phosphorus, arsenic, boron, lead, zinc, bismuth, tin, and carbonaceous substances, *e.g.*, plain lubricating oil, are specially mentioned. Gentle ignition of the mixed nitrates followed by reduction at a low temperature ($< 500°$) and subsequent cooling in a current of pure ammonia is the most usual method of preparation.

Such catalysts, it is stated, exert considerable activity at 450°, but are usually operative at 500–600°.

The early units constructed for containing the catalyst were apparently externally heated, but owing to the weakening of the furnace walls by the action of the hot hydrogen on the steel, with the subsequent liability to explosion, internal electrical heating was adopted.

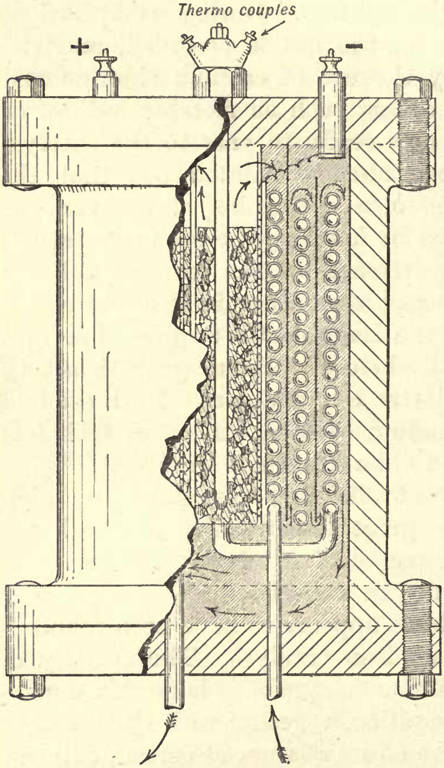

FIG. 18.

The modern furnaces probably follow Haber's earlier designs of experimental furnaces, (Fig. 18) in which the catalyst was contained in a thin steel vessel, the pressure being the same inside and out, all danger of collapse being thereby avoided. The tube was electrically heated and surrounded by a set of heat interchange coils, the whole being inserted in an internally lagged massive steel pressure container.

Since the reaction itself is exothermic (see *ante*) the supply of electric energy to be continuously supplied is but small and under certain conditions may be entirely dispensed with.

It will be evident that the difficulties of making large individual units necessitate that a given volume shall produce the maximum yield of ammonia per unit of time, the space time yield being all important.

The gases, after entering the catalyst furnace pass through the coils of the heat interchangers and enter the catalyst chamber at from 500–600°. From 3–7 per cent. conversion into ammonia is the actual transformation effected, depending on the various factors, such as (*a*) pressure, (*b*) temperature of operation, (*c*) how far equilibrium is established ; this in turn depending (i) on the activity of the catalyst at the temperature employed, and (ii) on the time of contact of the gas with the catalyst. The effluent gases, having given up most of their heat when passing over the heat interchanger system of tubes, leave the furnace.

It is evident that the conversion is relatively so small that the unchanged gases cannot be allowed to escape. A circulatory system is therefore necessary. Accordingly, the ammonia is more or less partially removed from the gases whilst still under pressure either by liquefaction or by absorption by water on the counter-current system. The gases are then dried, passed over palladium asbestos to remove any traces of oxygen accidentally admitted by the circulating pump or from the water, and then returned to the catalyst furnace. The pressure on the circulating system is continually maintained by the admission of fresh purified gas.

The inert gases (argon and methane) will naturally accumulate in the system, and must be blown off, causing the simultaneous loss of both hydrogen and nitrogen, which must be replaced by fresh gas.

It will be noted that, apart from the exceedingly important questions of grain size of catalyst, the requisite optimum interstitial velocity (governing the actual shape of the catalyst chamber), and the efficiency of thermal regeneration, the maximum output per unit of volume at any given temperature will depend on two factors, viz., catalytic activity and velocity of gas circulation. It has been shown that nearly 25 kilos. of ammonia can be produced per hour per litre of catalyst space at 150 atmospheres when uranium is used as catalytic material (at a temperature of 550°) with a circulation velocity of 10^6 litres per hour of gas per litre of catalyst space. According to published information, equally good results may be obtained with an activated iron catalyst when slightly higher temperatures and higher circulation velocities are employed.

Under these conditions, equilibrium concentrations are not obtained, but, nevertheless, the product, ammonia concentration × volume of gas treated per hour, is a maximum, the output falling as the speed is either increased or diminished. The chief limitations to high circulation velocities are to be found in the technical design of an efficient high speed heat interchanger. An alternative method of development would entail the use of very low speeds, with a catalyst operating at the lowest possible temperatures; under these conditions, the conversion would be extremely large with a corresponding rise in the thermal effect. Patents of the General Chemical Co., U.S.A., appear to forecast such a procedure. The necessity for internal heating and any complicated form of heat interchange would be dispensed with, two factors which might go far to minimise the lower hourly yields obtained from a given volume of catalyst space.

As in most catalytic operations, no general formulation of the mechanism of catalysis can be laid down, but the following points may be noted in connection with this process.

(1) The most active catalytic metals are those possessing a high molecular weight.
(2) Surface absorption is not the only factor involved, since the alternate passage of hydrogen and nitrogen over the catalytic material will give good yields of ammonia.
(3) The formation of both nitrides and hydrides has been shown to occur with many of the catalysts employed.

Either on the "adsorption" or "intermediate compound" theory, the function of the promoter is evidently based on its power of correcting the composition of the absorbed layer or forming the correct nitride hydride complex in the catalyst mass.

THE CATALYSTS EMPLOYED IN THE PREPARATION OF CYANAMIDE

In 1894, Moissan showed that calcium carbide when pure could not absorb nitrogen[1] up to 1200°, but in the next year

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[1] *Compt. rend.*, 1894, 1918.

Frank and Caro's experiments on technical carbides containing the usual impurities showed that rapid absorption could be obtained below 1100°, and thus laid the foundation of a very large industry. It was at once evident that the presence of catalytic substances materially hastened the process of absorption and permitted the reaction to proceed at a lower temperature. This latter point is specially important, as the absorption of nitrogen by alkali and alkaline earth carbides proceeds by two reversible reactions :

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C$$
$$CaC_2 + N_2 \rightleftarrows Ca(CN)_2$$

The quantity of cyanide formed always increases as the temperature is elevated, but is practically negligible in amount for calcium carbide up to 1100°. Any effective lowering of the temperature employed will thus effect an economy in the utilisation of both heating energy and nitrogen, as well as a simplification of the technical operations.

It was not until 1906, however, that the utility of adding any specific catalytic material to hasten the absorption of nitrogen was suggested. Carlson[1] proposed the use of calcium fluoride, and Polzenius that of the chloride.

The subject was carefully investigated by Bredig and Fränkel,[2] who determined the effect of the addition of 10 per cent. of catalytic material on the quantity of nitrogen absorbed in two hours at various temperatures. At 800°, the addition of 10 per cent. of calcium chloride effected a 22 per cent. absorption, whilst 10 per cent. of lithium chloride effected 17 per cent. absorption, the carbide alone only absorbing some 3 per cent. The chlorides of the other elements of the alkalies and alkaline earths were not so active, their efficiency falling off with the increase in their atomic weights.

From these and other investigations, it appears that the chief function of the catalyst is to act as a fusible solvent for the calcium carbide. Not only does the absorption of nitrogen proceed more rapidly in the flux, but at the same time fresh surfaces of the unfused calcium carbide are expressed to the action of the nitrogen by the removal of the reaction products.

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[1] *Chem. Zeit.*, 1906, **30**, 1261.

[2] *Zeitsch. Elektrochem.*, 1907, **13**, 69, 605 ; 1908, **14**, 565.

According to Foerster and Jacoby, the unchanged lime in the commercial carbide also exerts a catalytic activity by producing incipient softening at 1100°, thus offering an explanation of Moissan's results. Calcium chloride has a greater solvent action on the carbide than calcium fluoride, possibly on account of its lower melting point, and is thus a more effective catalyst.

The use of potassium carbonate (4 per cent.) has been suggested by Pollaci,[1] whilst recently the use of the relatively cheap sodium chloride has been advocated as the most suitable catalyst for operation on a technical scale. But little is known about the solubilities of calcium carbide, cyanamide, and nitrogen in these various solvents, and no determinations appear to have been made on the velocities of the reaction in such solvents, subjects which might very well repay investigation.

CATALYSIS IN THE PREPARATION OF NITRIDES

The only technical production of nitrides from atmospheric nitrogen was accomplished by Serpek in the Savoy. Although certain difficulties militated against the economic success of his earlier plants, yet, on account of the apparent possibilities of some such process, some allusion must be made to Serpek's work.

Serpek's process was based upon the following reactions, obtaining aluminium nitride by the simultaneous reduction and azotisation of the oxide :

$$2Al_2O_3 + 6C \rightleftarrows 4Al + 6CO$$
$$4Al + 3C \rightleftarrows Al_4C_3$$
$$4Al + 2N_2 \leftrightarrows 4AlN$$

Caro's investigations have shown that the dissociation temperature of the nitride is higher than that of aluminium carbide, and consequently the nitride is actually formed through the intermediary of the metal.

The optimum temperature for nitrogen absorption was found to be between 1800° and 1900° ; above 2000°, dissociation of the nitride commences.

Serpek's later experiments indicate that the temperature

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[1] *Zeitsch. Elektrochem.*, 1908, **14**, 565.

for rapid azotisation could be considerably reduced by the addition of certain catalytic material. His earlier claims as to the efficacy of the addition of small quantities of hydrochloric acid or sulphur dioxide to the nitrogen could not be substantiated, but a small quantity of hydrogen appears to exert a considerable catalytic activity. More important is the addition of catalysts to the solid reacting phase, such as the addition of small quantities of copper, iron, or manganese to the alumina. Serpek obtained good results with natural French bauxite rich in iron. Tucker and Read[1] confirmed these observations of Serpek. Fränkel[2] conducted a series of experiments on the relative activities of various forms of carbon, and arrived at the conclusion that finely divided carbon, such as soot, was most effective, rapid absorption taking place between 1500° and 1600°.

It will be noted that if the series of reactions given above actually represent the various equilibria between the different phases then the ratio :

$$\frac{(CO)^6}{(N_2)^2} \text{ or } \frac{(CO)^3}{(N_2)}$$

should be constant. This was actually shown to be the case by this investigator, who found that with increasing temperatures the equilibrium concentration of carbon monoxide rose, as is indicated in the following table. Total pressure 1 atmosphere.

Temperature.	$K = \frac{(CO)^3}{(N_2)}$	Per cent. CO equilibrium (mean figures).
1500°	500	33
1600	4,500	57
1700	16,900	75

It will be noted that for low temperature operation the gas must be as free as possible from carbon monoxide, thus limiting the employment of generator gas as a source of nitrogen.

The Badische Co., in a series of patents,[3] protect the use of catalytic agents other than copper and iron, and more especially the oxides of those elements which form stable nitrides, on reduction and azotisation, such as chromium, uranium, vanadium, molybdenum, zirconium, titanium, and silicon.

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[1] *Trans. Amer. Electrochem. Soc.*, 1912, 22, 67.

[2] *Zeitsch. Elektrochem.*, 1913, 19, 362.

[3] D.R.P. 243839, 235300 *et seq.*

THE CYANIDES

The recently published investigations of Bucher[1] on the use of finely divided iron as a catalyst in the absorption of nitrogen by a hot mixture of sodium carbonate and coke for preparing sodium cyanide has led to an increased amount of attention being given to the old, and as yet unsolved, problem of the economic absorption of nitrogen to form cyanides. Since the market value of fixed nitrogen in the form of cyanide is greatly in excess of its actual value on the nitrogen content as a fertiliser, repeated attempts have been made to replace the somewhat costly Castner process, which utilises expensive raw materials such as sodium and ammonia, by some method in which atmospheric nitrogen could be utilised.

In reality, this problem had long received a great deal of attention by various investigators, and it remains to the credit of Possoz and Boissière that they erected the first nitrogen fixation factory in the world at Newcastle in 1843. The process utilised was one which even then had long been known, viz., the reaction between alkalies and alkaline earths with carbon and nitrogen to form cyanides at high temperatures, as was noted by Deforres in 1828, by Clark in the Clyde furnaces (in which potassium cyanide was isolated) in 1835, and later by Bunsen and Playfair in 1845.[2]

The formation of sodium cyanide occurs according to the following equation :

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO.$$

Very high temperatures are required to produce even a small conversion. To obviate the difficulties attendant on the use of high temperatures and to obtain a more reasonable conversion, the employment of various catalytic materials was soon suggested.

Thompson, in 1839, directed attention to the catalytic effect of finely divided iron. The catalytic effects of other metals, especially manganese and chromium, were noted by Margueritte and Sourdeval in 1860, and by Swan and Kendall in 1845. Bucher has recently reinvestigated Thompson's

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[1] *J. Ind. Eng. Chem.*, 1917, **9**, 233.

[2] *Rep. Brit. Assoc.*, 1845, 185.

process, and claims to obtain the rapid absorption of nitrogen in producer gas at a temperature of 900° by briquettes containing sodium carbonate, coke, and iron as a catalytic material. Margueritte and Sourdeval[1] suggested the use of barium carbonate, instead of sodium or potassium, as absorption of the nitrogen is more rapid. Readmann, in 1895, developed the process and obtained good technical yields of barium cyanide according to the equation :

$$BaO + 3C + N_2 = Ba(CN)_2 + CO$$

The optimum temperature of absorption was stated to be 1400°. Swan and Kendall, a few years later, modified the process by the addition of certain catalysts, such as the oxides of titanium, molybdenum, chromium, and manganese, to the charcoal–alkaline-earth mixture before the absorption of the nitrogen. It is stated that with these catalysts the formation of cyanide will commence at a dull red heat.

At the present time no technical process for the preparation of cyanides by these methods is in operation. The reactivity of the fused alkalies towards all materials capable of withstanding the high temperatures and the difficulties associated with the removal of a partly fused mass of cyanide from furnaces appear to militate against successful operation. The United States Government, however, has made a substantial monetary grant to defray expenses connected with such technical investigations as may be necessary.

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[1] B.P. 1027/1860.

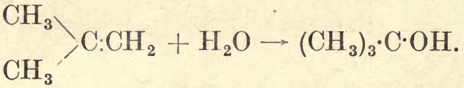
CHAPTER VIII

HYDRATION AND HYDROLYSIS

HYDRATION

Simple hydration, or the direct addition of water by compounds, is a reaction which in certain cases may be promoted by catalytic agents. In the main, such reactions are confined to the fixation of water by unsaturated organic compounds with the production of oxygen-containing derivatives. Thus, from unsaturated hydrocarbons, alcohols, aldehydes, and ketones may result. Similarly, careful hydration of certain nitriles will yield the corresponding amides, and, in a few cases, the hydration of imides has been noted. As a class, catalytic hydration processes have, hitherto, been unimportant technically, but recent developments in the synthetic production of alcohol from carbide as starting point may give them a considerable importance in future application.

As with the processes of hydrolysis subsequently to be described, the mineral acids are active agents in promoting catalytic hydration. The transformation of isobutylene to trimethylene carbinol is accomplished in the cold in presence of sulphuric acid of moderate dilution.[1]



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{:}CH_2 + H_2O \rightarrow (CH_3)_3{\cdot}C{\cdot}OH.$$

Earlier still, the addition of water to pinene was shown to occur in presence of dilute nitric acid.[2]

$$C_{10}H_{16} + 3H_2O \rightarrow C_{10}H_{22}O_3.$$

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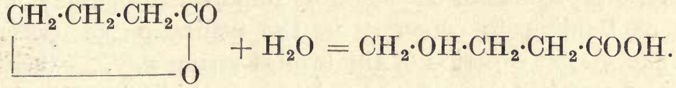
[1] Butlerow, *Annalen*, 1867, **144**, 22.

[2] Wiggers, *Annalen*, 1846, **57**, 247.

Similarly, hydrochloric acid accelerates the addition of water to crotonic aldehyde[1] according to the equation :

$$CH_3\cdot CH{:}CH\cdot CHO + H_2O \rightarrow CH_3\cdot CH\cdot OH\cdot CH_2\cdot CHO,$$

yielding the corresponding hydroxybutyric aldehyde. The processes of Wilson and Milly, previously cited in the discussion of hydrogenation of oils, also belong to this class of reaction, since, under the influence of sulphuric acid, iso-oleic acid, which is liquid, is transformed by addition of water to solid oxystearic acid. The reversibility of certain dehydration processes catalysed by acids, as, for example, the catalytic conversion of hydroxy-acids to lactones, also points to the catalytic activity of acids in simple hydration processes. The case of γ-butyrolactone formation from γ-hydroxybutyric acid studied by Henry[2] is an example in point, dilute acids being the catalytic agent :



$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\cdot CO\\ \qquad\qquad\qquad\qquad O\end{array} + H_2O = CH_2\cdot OH\cdot CH_2\cdot CH_2\cdot COOH.$$

The point has recently been specially tested by Johannson and Sibelius[3] with confirmatory results, although a remarkable conclusion, however, is reached in that the hydration of β-lactones is apparently not catalysed by hydrogen ions. Nor, as was demonstrated by Rivett and Sidgwick,[4] is the hydration of acetic anhydride catalytically accelerated by hydrogen ions.

Synthetic alcohol.—In the development of processes for the synthetic production of alcohol, the possibility of utilising a process of hydration has been studied. The necessities of war and the great requirement of alcohol for the manufacture of munitions has stimulated investigation. In England, alcohol is mainly obtained by fermentation processes from grain. In Germany, production from potatoes by a combined hydrolytic and fermentation process has been largely used in addition to the grain fermentation process. The United States has developed a combined hydrolytic and

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[1] Wurtz, *Bull. Soc. chim.*, 1884, (ii), **42**, 286.

[2] *Zeitsch. physikal. Chem.*, 1892, **10**, 98.

[3] *Ber.*, 1918, **51**, 480.

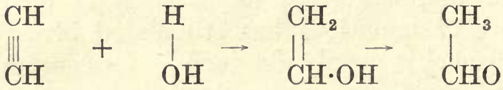
[4] *J. Chem. Soc.*, 1910, **97**, 732.

fermentation process, utilising sawdust as source of carbohydrate, whilst the Scandinavian countries and, more recently, Germany have devoted attention to alcohol recovery from the waste-liquors in the sulphite-cellulose process. Nevertheless, the demand for alcohol is increasing so rapidly, more especially with a view to its use as a fuel for internal combustion engines, that the synthetic production from cheap carbide is not without industrial possibilities. Indeed, it has been recently stated that successful production has now for some time been carried on by the Hoechst Farbwerken in Germany and that a Swiss company, the Longa Elektricity Works at Visp, Switzerland, will soon be able to cover the alcohol requirements of their country with the synthetic product. The consumption of industrial spirit is increasing rapidly in England, and reached in 1916–1917 a total of upwards of four million gallons. It is obvious that the development of a synthetic process is of considerable importance in this country also, as tending to economy in the utilisation of potential food supplies at a period of the utmost stringency.

Acetylene, obtained from calcium carbide by treatment of the latter with water, is the starting point of the synthesis as developed in Germany and Switzerland. By a catalytic process of hydration, the acetylene is next converted into acetaldehyde according to the equation :

$$\mathrm{CH{\vdots}CH + H_2O = CH_3{\cdot}CHO.}$$

The operation is presumably a two-stage reaction, the unsaturated alcohol first produced by simple addition of water changing by the ordinary shift of the labile hydrogen atom to an aldehyde, according to the scheme :



$$\begin{matrix} \mathrm{CH} & & \mathrm{H} & & \mathrm{CH_2} & & \mathrm{CH_3} \\ ||| & + & | & \rightarrow & || & \rightarrow & | \\ \mathrm{CH} & & \mathrm{OH} & & \mathrm{CH{\cdot}OH} & & \mathrm{CHO} \end{matrix}$$

The aldehyde thus obtained is available for hydrogenation to yield alcohol (p. 187), or alternatively, may be oxidised to acetic acid (p. 133) for utilisation as such, or for subsequent conversion of acetic acid to acetone (p. 311).

Various catalytic agents in different media have been suggested with the view of accelerating the hydration of the acetylene. Especially in most recent years has the patent literature of this process grown. In the main, the various proposals suggest the conduct of the reaction by leading the gas into a warm liquid medium generally containing dissolved in it a suitable metallic salt to act as accelerator. Thus, according to the Griesheim Elektron Co.'s French Patent No. 474246/1915, the acetylene is to be led into hot 20–25 per cent. sulphuric acid, or 30–35 per cent. phosphoric acid, or organic sulphonic acids, all in presence of the corresponding mercury salts. The British Patent No. 5132/1915 suggests the passage of acetylene into glacial acetic acid at 80–90° containing a dissolved mercury salt, the necessary water to be added as required. Meister, Lucius, & Brüning in U.S. Patents 1151928 and 1151929/1915 suggest the addition of ferric salts, *e.g.*, sulphate, to the acid solution of the mercury salt, together with a hexavalent chromium compound, *e.g.*, chromic acid, in order to hinder the separation of mercury from the solution. D.R.P. No. 293070/1916, of the same firm, recommends as medium for the process, metallic mercury in dilute acids. The Union Carbide Co., in U.S. Patents, Nos. 1213486 and 1213487 of 1917, claim for the passage of acetylene into a solution of dilute sulphuric acid, a mercury salt and the salt of a weak acid, *e.g.*, a borate, or, alternatively, into a solution of the mercury salt and the acid salt of a strong acid, *e.g.*, a bisulphate. The French Patent, No. 479656/1916, of H. Dreyfus claims for the passage of acetylene and water into solvents, (*a*) in which the mercury salt is soluble, *e.g.*, acetic acid, or (*b*) in which acetylene is soluble, *e.g.*, acetone. The aldehyde formed is to be converted direct into acetic acid by means of oxidising agents or by air in presence of catalysts such as cerium oxide, vanadium pentoxide, copper acetate, permanganates, manganese or copper nitrate, or platinum–palladium sponge. The oxidation to acetic acid is also claimed in the Badische Co.'s patent, D.R.P. 294724/1917, using atmospheric air in presence of iron salts and organic salts of alkalies and alkaline earths, including magnesium and aluminium. It is claimed that in this way the oxidation proceeds in the cold and no per-acids are formed. It is the formation of these latter which renders dangerous and uncertain the operations at present in use technically for the conversion of aldehyde to acetic acid, in which oxygen under pressure is used as oxidising agent in presence of such a catalyst as manganous acetate.

HYDROLYSIS OF SUGARS AND ESTERS

Processes of hydrolysis, that is to say, the process of resolution of a compound into two products with the simultaneous introduction into the resulting compounds of the component hydrogen and hydroxyl groups of water, have long been known to be sensitive to catalytic acceleration. Wilhelmy, in 1850, showed the catalytic influence of acids in the hydrolysis or " inversion " of cane-sugar according to the equation :

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6},$$

by a study of the reaction velocity with which the process proceeded. This velocity could be determined with ease, as the progress of the reaction was accompanied by a change in the optical rotatory power of the system, not only in degree, but also in sign. Hence the term " inversion " of cane-sugar.

Similarly with esters, their hydrolysis to alcohol and acids may, in many cases, require years for completion if water alone is employed as the hydrolytic agent. On the contrary, in presence of small quantities of mineral acids, hydrolysis may be completed in a few hours, and all acids behave in like manner though in varying degree. This catalytic influence of acids is also found in the hydrolysis of other organic compounds, such as amides, acyl derivatives, and ketonic acids. As, in general, such reactions proceed slowly, the rate of progress is susceptible of careful measurement, and consequently they have formed suitable material for the investigation of catalytic processes.

The inversion of cane-sugar, which may be taken as the type of all hydrolyses of various sugars and carbohydrates, has been investigated, since the work of Wilhelmy already cited, by numerous observers. Wilhelmy showed, experimentally, that the velocity of inversion at any moment was proportional to the concentration of the sugar at that moment. This discovery was made prior to the formulation of the law of mass action, and is an experimental consequence thereof, provided that the water is present in large excess and changes only negligibly in concentration during the reaction. The mathematical expression of this unimolecular process is given by the equation :

$$\frac{dx}{dt} = K\,(a - x),$$

where a is the original concentration of sugar and x the amount converted in time t. On integration the equation becomes

$$K = \frac{1}{t} \log \frac{a}{a - x},$$

from which, with the aid of the experimental determinations, reaction velocity constants may be calculated. The progress of the change in sugar inversion as well as in ester hydrolysis is readily followed, by polarimetric determinations in the former, and by determination of the increase of acidity of the solution in the latter case.

The catalytic activity of acids upon the two reactions was studied by varying the concentration and nature of the acid employed. The researches of Löwenthal and Lennsen (1862), of Fleury (1876), of Ostwald (1884), and of Spohr (1885–1888) gave Arrhenius (1889) abundant material upon which to base his deductions concerning the part which acids played in the catalytic process. It was readily shown that increase in concentration of the acid gave increased velocity of inversion, the increase being roughly, though not exactly, proportional to the increase in concentration. It was further demonstrated that, in equal concentrations, different acids varied greatly in their catalytic activity.[1] This was greatest with the strong mineral acids investigated. Thus, a 0·5 normal solution of hydrochloric acid catalysed the inversion 250 times more rapidly than acetic acid of the same normality. Closely parallel results were obtained in a study of the corresponding hydrolysis of esters using such acids.

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[1] Ostwald, *J. pr. Chem.*, 1883, **27**, 1.

It is common knowledge how this behaviour of acids towards sugar inversion and ester hydrolysis was coupled, by Arrhenius, with his observations upon the electrical conductivity of aqueous solutions of acids, and how, as a result, the theory was developed that the catalytic activity of acids was due to the hydrogen ions which acids yielded when in solution. The strong mineral acids, according to the theory, possessed a high catalytic activity, because in solution their dissociation into ions was practically complete. Conversely, with weak acids, feebly dissociated, the catalytic activity was small.

The effect of the addition of a neutral salt of a weak acid upon the catalytic activity of the acid assisted considerably in the development of the dissociation theory. Arrhenius was able to show that the addition, for example, of sodium acetate to a solution of acetic acid enormously depressed the catalytic activity of the acid. Thus a 0·25 normal solution of the salt, when added to a solution of the acid of the same normality, reduced its activity in the ratio of 0·74 : 0·0105. Assuming that the addition of sodium acetate repressed the degree of dissociation of acetic acid and therefore the hydrogen-ion concentration in accordance with the law of mass action, the calculated variation in the reaction velocity should be in the ratio 0·74 : 0·0100, a remarkably close agreement with the experimentally determined figures. Accumulating evidence of such nature led rapidly to the acceptance, not only of the hydrogen-ion theory of acid catalysis, but also to acceptance of the dissociation theory itself.

With strong acids, the quantitative factors were by no means so readily explicable. Exact proportionality between the hydrogen-ion concentration, as calculated from electrical conductivity, and the catalytic activity does not obtain in solutions of strong mineral acids, except, as was demonstrated by Palmaer,[1] in extremely dilute solutions. The increase in activity is always somewhat greater than the increase in hydrogen-ion concentration as determined by electrical conductivity measurements. Moreover, the influence of neutral salts of strong acids is very remarkable. It is found, for example, that in ester catalysis the addition of a normal

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[1] *Zeitsch. physikal. Chem.*, 1894, 22, 492.

solution of potassium chloride accelerates the catalytic activity of a 0·1 normal solution of hydrochloric acid by as much as 22 per cent., whereas on the simple dissociation theory, as with acetic acid, a diminution of reaction velocity would be expected. This interesting abnormality, the so-called neutral salt action, has occupied the attention of a considerable number of investigators down to the present day, and so far no completely satisfactory explanation of the phenomena is forthcoming.

It has been frequently shown, and especially by Poma[1] in an extended series of measurements, that in ester catalysis the influence of neutral salts on the velocity of reaction depends in high degree on the nature of the anions, and that the influence of the cations is either non-existent or within the limits of experimental error. Thus, the chlorides of potassium, sodium, lithium, barium, strontium, and magnesium cause the catalytic power of the hydrochloric acid to be enhanced to approximately the same degree in equal concentrations of salt. Further, the influence of salts differs in degree with the cation employed. In descending order of accelerating effect come the chlorides, bromides, nitrates, and iodides, when used with the corresponding acid. This observation may be extended to all acids by stating that the accelerating action diminishes with diminishing degree of dissociation as calculated by conductivity methods and finally becomes, with weak acids, not an acceleration but a retardation, as previously mentioned in the case of acetic acid.

Early suggestions of Arrhenius to account for neutral salt action are twofold. It was assumed[2] that there exists in solution an equilibrium between the active and inactive forms of the substrate, and that this equilibrium was displaced by increase of ionic concentration in the direction of increase of active modification, thereby resulting in increase of reaction velocity. An attempt at precise differentiation between active and inactive molecules in chemical change has recently been made in the previously discussed papers, by Lewis[3] in which papers the concepts of critical energy and critical increment of energy necessary to produce reaction

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[1] *Gazzetta*, 1911, **41**, 353.

[2] *Zeitsch. physikal. Chem.*, 1889, **4**, 226.

[3] *J. Chem. Soc.*, "Studies in Catalysis," Parts I–IX, 1914–1918.

are introduced. The active molecules are assumed to differ from the inactive in respect of their internal energy, which is considerably greater than that possessed by an average molecule of the substance at the temperature in question. The fact that the critical energy is high indicates that only a very small fraction of the total molecules will be active at any moment. In the second place, Arrhenius suggested that the ions of the neutral salt have some action on the hydrogen ions of the acid and thereby contribute to increased activity.[1] For strong acids alone, this could be formulated by an equation of the form :

$$K = a(\mathrm{H}^{\cdot}) + b(\mathrm{H}^{\cdot})^2$$

where K is the velocity constant.

Lunden[2] extended this idea to the mathematical interpretation of the experimental results in presence of neutral salts.

A considerable body of opinion has sought the explanation of the accelerating influence of neutral salts by attributing to the latter a concentrating effect on the acid catalyst, due to withdrawal of solvent water from the solution. The solvate theory of H. C. Jones in America is capable of such application. In England, an investigation of the processes operative in solution by H. E. Armstrong and his co-workers has been animated with a similar view-point. In particular, the studies of Caldwell,[3] Whymper,[4] Armstrong and Watson,[5] Worley[6] may be mentioned in this connection. The view is put forward that hydrolysis is an associative process involving the interaction of associated complexes, the hydrated hydrolyte and hydrated catalyst. By studies of the inversion of sucrose and of the hydrolysis of esters, the apparent molecular hydration values of acids and neutral salts have been determined and the accelerating influences observed in the study of reaction velocity are attributed to such agencies. The theory as developed is directly opposed to the generally accepted electrolytic dissociation theory, and it is claimed[7] that the

[1] *Zeitsch. physikal. Chem.*, 1899, **28**, 329.

[2] *Ibid.*, 1904, **49**, 189.

[3] *Proc. Roy. Soc.*, 1906, (A), **78**, 272.

[4] *Ibid.*, 1907, (A), **79**, 576.

[5] *Ibid.*, 1907, (A), **79**, 579.

[6] *Ibid.*, 1912, (A), **87**, 604.

[7] See especially Worley, *Phil. Mag.* (1914).

facts disclosed go far to show that this hypothesis is no longer tenable. The associative theory has earned, however, considerable criticism. Thus, Senter[1] directs attention to the fact that the relative neutral salt action of different salts is not that of their ordinary degree of hydration. Further, the relatively slight influence of temperature on neutral salt action[2] is, according to Senter, in marked contradistinction to the general effect of temperature on hydration.

An accumulation of evidence during recent years has given support to the theory that, in homogeneous liquid systems, the undissociated molecule of a catalytic substance, in addition to the ions, possesses a certain definite catalytic activity, which, in a given reaction, bears a definite relation to that of the ion which is catalytically active. Researches of Senter,[3] of Acree and Nirdlinger,[4] and of Lapworth[5] directed attention to the general principle involved, while, in the last-named research, the special application to hydrogen chloride was pointed out in connection with the work on the effect of water on the activity of acids in alcoholic solution. Researches of Goldschmidt on catalytic esterification by acids in alcoholic solution (p. 295), of Acree and his co-workers[6] on numerous reactions both catalytic and non-catalytic, of Bredig, Millar, Braune, and Snethlage on the catalytic hydrolysis of diazoacetic esters (p. 282), have, more recently, yielded contributory evidence to the view-point that undissociated molecules might possess a specific catalytic activity. Reviewing the available data, Snethlage was led to suggest,[7] in reactions catalysed by acids, and therefore in ester hydrolysis and the inversion of cane-sugar, that the greater the strength of the catalysing acid the greater is the catalytic activity of the un-ionised portions as compared with the activity of the ion. If one assumes that the reaction velocity is composed of two velocities determined by the catalytic activity of

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[1] *J. Chem. Soc.*, 1907, **91**, 462.

[2] See Taylor, *J. Amer. Chem. Soc.*, 1915, **37**, 551.

[3] *J. Chem. Soc.*, 1907, **91**, 460.

[4] *Amer. Chem. J.*, 1907, **38**, 489.

[5] *J. Chem. Soc.*, 1908, **93**, 2197.

[6] *Amer. Chem. J.*, 1912, **48**, 352.

[7] *Zeitsch. Elektrochem.*, 1912, **18**, 539; *Zeitsch. physikal. Chem.*, 1913, **85**, 211.

molecule and of ion acting in proportion to their concentration, the velocity may be expressed by the equation :

$$R = n_{\dot{H}}K_{\dot{H}} + n_mK_m,$$

where n refers to the concentration, K to the catalytic activity of ion or molecule, $_{\dot{H}}$ or m.

With such an assumption it is possible to formulate more completely in a comprehensive theory the phenomena of ester hydrolysis, sugar inversion, or other acid catalytic reactions, as well as the apparently anomalous results obtained with strong acids and the so-called neutral salt action. For, utilising such a concept of dual activity, it emerges on examination that with a weak acid such as acetic acid the activity of the molecule is negligible as compared with that of the hydrogen ion. The stronger the acid the more preponderating becomes the *rôle* of the undissociated molecule, until with a strong acid such as hydrochloric acid it is calculable from experimental data with the above equation that the undissociated molecule is actually more active catalytically than the hydrogen ion. This would explain the proportionately greater increase with strong acids of the rate of hydrolysis of esters, or of cane-sugar inversion with increase of hydrogen-ion concentration, since the molecular concentration is also increasing simultaneously. Similarly, since addition of neutral salts suppresses the degree of dissociation of the acids, an increase of reaction velocity would be expected in the case of all such acids as have undissociated molecules more active catalytically than the hydrogen ion resulting from their dissociation. The theory when applied by Taylor to ester catalysis by hydrochloric acid with and without addition of neutral salts gave results[1] showing that the activity of the hydrochloric acid molecule was approximately twice as great as that of the hydrogen ion. With trichloroacetic acid, the ratio of the two activities $K_m : K_H$ was approximately 1 : 3, whilst with the weaker acid, dichloroacetic acid, the ratio was still lower. The constancy of the activity of the hydrogen ion from different acids in a given reaction and the varying activity of the undissociated molecule is well illustrated by

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[1] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, 2, No. 37.

the results of Dawson and Powis[1] on the catalytic activity of acids in the keto-enol tautomerism of acetone, which are collected in the following table :

Acid catalyst.	K_H	K_m	$K_m : K_H$	Affinity constant
Hydrochloric	440	780	1·77	—
Dichloroacetic	,,	220	0·50	$5·1 \times 10^{-2}$
l-β-Dibromopropionic	,,	67	0·152	$0·67 \times 10^{-2}$
Monochloroacetic	,,	24·5	0·055	$0·155 \times 10^{-2}$
Acetic	,,	1·5	0·0034	$0·0018 \times 10^{-2}$

This dual theory of catalytic activity is being developed continuously, and a large and increasing literature upon the subject is accumulating.[2] As yet it is impossible to state in what directions the theory will develop or how far it will generalise the various factors observed in such reactions.

The catalytic activity of the acid in such reactions as ester hydrolysis is now fairly generally attributed to the formation of intermediate additive compounds. The systematic investigation of the formation of such compounds has recently been undertaken by Kendall and his co-workers,[3] and the results obtained are not without significance in the interpretation of strong acid catalysis and neutral salt action. By the examination of a number of ester-acid systems, using a freezing-point method, it was shown that the formation of oxonium compounds between ester and acid followed the same general principles obtained in earlier work on compound formation in other organic systems. For example, combination is most marked between strong acids and esters of weak acids. Further, the extent of compound formation decreases with decrease of acid strength, although, even with the weakest acid, compound formation was indicated by the form of the curves, without, however, any isolation of the compound. By making the radicals R and R_1 of the ester $R·COOR_1$ more negative, the degree of compound formation also diminishes. The concordance of these results with the facts of catalytic activity previously put forward is sufficiently obvious to

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[1] *J. Chem. Soc.*, 1913, **104**, 2135.

[2] See *Annual Reports on the Progress of Chemistry*, London Chemical Society, Vols. X to XIV, 1913–1917.

[3] See *J. Amer. Chem. Soc.* 1916, **38**, 1712.

prompt the conclusion that the hypothesis of the intermediate additive compound is fundamentally sound.

The dependence of the velocity of hydrolysis of esters in presence of catalysing acids on the nature of the ester substrate was extensively investigated by Lowenherz,[1] who showed that the influence of the alcohol radical of the ester was comparatively slight, but that the velocity was to a marked degree dependent on the nature of the ester acid. Thus, ethyl formate hydrolyses twenty times more rapidly than ethyl acetate; the velocities with methyl, ethyl, and propyl acetates are all approximately equal to one another, whereas with the homologous series of esters of acetic, propionic, butyric, and valeric acids, the velocity of hydrolysis becomes increasingly slower with increasing complexity of acid, that of the formate being one hundred times greater than the velocity of hydrolysis of the valerate. With aromatic esters, the velocity is even slower. Ethyl acetate hydrolyses one hundred and fifty times more rapidly than ethyl benzoate with the same concentration of catalysing acid.

Alkaline hydrolysis of esters.—The resolution of an ester into hydrolytic products may also be accelerated by the use of alkalies. In this case, the acid produced by hydrolysis is immediately neutralised by the alkali present, giving the corresponding alkali salt of the acid. The net result of the process may be represented by the general equation:

$$\mathrm{R{\cdot}COOR_1 + M{\cdot}OH = R{\cdot}COOM + R_1OH.}$$

Thus, in the course of the reaction, both ester and alkali disappear, the reaction proceeding until one or other constituent is completely used. Obviously, also, the reaction is bimolecular and the reaction velocity equation is of the form

$$\frac{dx}{dt} = k(a - x)\,(b - x)$$

where a and b are the concentrations of ester and alkali, and x the amount of each transformed at time t. Expressed in the integrated form, this equation gives

$$k = \frac{1}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

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[1] *Zeitsch. physikal. Chem.*, 1894, **15**, 389.

with which the reaction constant k can be calculated from the measurements of the concentrations of the reacting substances. As in the process of reaction the alkali is converted to a neutral salt, the velocity with which the action proceeds can be determined by titration with standard acid.

In this manner, Reicher was able to study[1] the velocity of hydrolysis, or saponification, as it is better expressed when speaking of alkaline hydrolysis, of esters in presence of sodium, potassium, and calcium hydroxides. It was demonstrated that in dilute solutions of alkali the velocity of saponification was independent of the nature of the base, proportional, however, to the alkalinity of the solution. These results led later to the conclusion that the hydroxyl ion was the active hydrolytic agent; that, moreover, the reaction was truly catalytic in nature, the catalyst, however, being removed from the system by the subsequent and independent interaction of the base with the acid formed by hydrolysis.

The relation of velocity of saponification to constitution of ester has from Reicher's experiments onward attracted considerable attention. The influence of the alcohol is apparently more marked than in the case of hydrolysis by acids, isobutyl acetate being hydrolysed only one-half as rapidly as methyl acetate in the same strength of alkali.[2] The influence of the nature of the acid radical is by no means so pronounced, however, since, with dilute soda at 14°, the velocity of saponification of the acetate is approximately double that of the isobutyrate, six times that of the isovalerate, and four times that of the benzoate. Later work[3] on the constitutional influence of the acyl grouping shows, however, that the velocity is determined largely by the complexity of the acyl group and more especially by substituents in close proximity to the carbonyl group. Assuming that hydrolysis is preceded by formation of an intermediate additive compound or ion complex, it may be deduced by analogy with the results of Kendall on acid hydrolysis, previously cited, that the

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[1] *Annalen*, 1885, **228**, 257.

[2] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, **1**, 110.

[3] Hjelt, *Ber.*, 1896, **29**, 1864; Kellas, *Zeitsch. physikal. Chem.*, 1897, **24**, 243; Sudborough and Feilman, *Proc. Chem. Soc.*, 1897, **13**, 243; Findlay and Turner, *J. Chem. Soc.*, 1905, **87**, 747; Gyr, *Ber.*, 1908, **41**, 4308; Findlay and Hickmans, *J. Chem. Soc.*, 1909, **95**, 1004.

strength of the acid forming the radical in the ester would also determine the velocity of the hydrolysis. Experimental test shows this to be the case.

The addition of neutral salts to systems of alkaline hydrolysis of esters may either repress or accelerate the velocity of saponification, as was shown by Arrhenius[1] and by Spohr.[2] The phenomenon of neutral salt action in alkaline hydrolyses is, however, much more obscure and unformulated than is the case with acid hydrolysis, the same regularities being by no means observable. Thus, in the hydrolysis of sodium chloroacetate by sodium hydroxide Senter showed[3] that the addition of salts accelerated the reaction. It is evident that each specific type of hydrolysis must be separately considered in this connection.

TECHNICAL APPLICATIONS

The hydrolysis of sugars and of polysaccharides, as well as of esters, finds extended technical application in several large industries. The whole soap industry is concerned with the hydrolysis of the fatty acid esters of glycerine, and, in the tallow industry, fatty acids are obtained by hydrolysis of the corresponding glycerides. The manufacture of glucose from starch is an example of the hydrolysis of polysaccharides and production of invert-sugar, whilst the degradation of cellulose by hydrolysis to fermentable sugars capable of yielding alcohol for industrial purposes is an industry of recent growth and of considerable promise for subsequent development. The more important scientific aspects of these technical applications merit individual discussion.

The manufacture of glucose.—The industrial development of catalytic hydrolysis of polysaccharides for the production of glucose has attained considerable proportions. As raw material for the preparation, starch or starch-containing materials are employed. In England, rice, rice starch, maize, and sago are chiefly used. Potato starch finds application in Germany. In America, the starch from maize or Indian corn is the principal material. All such materials yield,

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[1] *Zeitsch. physikal. Chem.*, 1887, **1**, 110.

[2] *Ibid.*, 1888, **2**, 1194.

[3] *J. Chem. Soc.*, 1907, **91**, 462.

with acids, products containing more or less of the glucose desired. The reaction occurring may be represented by the general equation :

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

As hydrolytic agents, dilute acids are employed, the acid functioning as catalyst. Various acids find technical application. In Europe, sulphuric acid is the usual reagent used. In America, hydrochloric acid is mainly employed. Other strong acids, such as nitric and phosphoric acids, may be employed if local circumstances are favourable to their use. Even sulphurous acid has been suggested as a hydrolytic agent.

Heat is always employed to assist the process of hydrolysis. Closed converters of cast-iron, copper, or gun-metal have replaced, almost entirely, the original lead-lined open converters made of wood. With the closed type of converter the temperature is maintained by injection of steam up to pressures of 30 lb.

With sulphuric acid, a 5 per cent. aqueous solution is employed in the open system. When pressure is simultaneously used, the percentage of acid may be reduced to as low as 0·5 per cent. Approximately two and a half times the weight of the acid solution is required for the hydrolysis of unit quantity of dried starch. In modern American practice, it is customary to employ large volumes of water with which a paste of the starch is made, and to which small quantities of pure hydrochloric acid are added to assist the hydrolytic process. The whole mass is subjected to a high temperature under pressure in massive copper converters.

Hydrolysis occurs in definite stages. After a short period of heating, the starch is completely converted to dextrins and maltose. At this stage, it no longer gives the blue coloration with iodine, but a reddish-brown coloration indicating the presence of a-dextrin. With further action of the acid, the dextrins and maltose yield glucose. The absence of the dextrin is determined by the non-appearance of a precipitate on addition of twice the volume of alcohol to a sample of the liquor. Care must be taken to avoid carrying hydrolysis too far, as glucose may itself be attacked by the acid liquor.

The process of hydrolysis may be stopped at any desired stage according to the product desired. If the syrup is required, the process is stopped immediately iodine gives a port wine colour to the solution. Consequently, corn syrup contains marked quantities of dextrin, averaging 40 per cent., with an equal quantity of glucose and 20 per cent. of water. Solid glucose is obtained from solutions which no longer yield the dextrin test, and the anhydrous sugar therefore generally contains less than 1 per cent. of this impurity, with not more than 5 per cent. of water.

Naturally, the time required for completion of the hydrolytic process is governed by the three factors: mean temperature during the operation, the pressures employed, and the concentration of the catalytic agent. The nature of the final product also governs the length of the process. For the solid product, the average time required is about 1½ hours; for the syrup, half this period or less.

After hydrolysis, the catalytic agent is removed by neutralisation with alkalies. For sulphuric acid, a milk of finely ground chalk in water is employed, the precipitated sulphate is allowed to settle, and the clear liquor drawn off. Soda ash is used in American practice, the mixture being left just faintly acid. Excess of alkali is avoided, as, even in small traces, it imparts coloration to the liquid in the subsequent operations. The filtered liquor is then partially concentrated and passed through bone-char filters, the resulting clear liquor being then concentrated in vacuum pans until the desired concentration is reached. On cooling, the mass crystallises.

Glucose from cellulose.—Wood cellulose may form a considerable source of glucose supplies in the future, and efforts to achieve the hydrolytic conversion on a technical scale have been numerous. The fuel problem for the motor industry has stimulated interest in the process, since the fermentable sugars produced can readily be employed in the manufacture of alcohol. The disintegration of cellulose is, however, a matter of great difficulty, and as yet it has not been so far generally developed as to compete commercially with the processes employing starch.

The various aspects of the problem have been presented somewhat as follows by F. W. Kressman of the U.S. Forest Products Laboratory, Madison, Wisconsin, and in a paper by the U.S. Department of Commerce, "By-products in the Lumber Industry." There is a large margin in the cost of raw material in favour of alcohol from wood waste as against alcohol from grain. The fuel charges of a wood waste installation are always a much smaller item than in the case of a grain distillery, since most saw-mills produce waste considerably in excess of their own power requirements. From wood waste, however, a yield of 20 gallons of proof spirit per ton of wood represents good practice as compared with 80 gallons per ton from corn. It is obvious, therefore, that the amount of material handled in certain parts of a plant producing alcohol from wood will be four times as great as in a grain distillery of equal capacity. Hence, the capital outlay and costs of operation will be somewhat greater. Portions of the plant, however, and among these the larger items, as, for example, the fermenter and the still equipment, will not need to be larger, so that one of the major costs of production will not be increased. The balance of points, it will be observed, is distinctly even, and with favourable conditions the wood alcohol industry may leap forward as a commercial success. Hitherto, this has not been realised except in particular cases.

The processes employed for the production of alcohol from wood may be classified in two groups, (*a*) hydrolysis of cellulose to fermentable sugars by means of dilute mineral acids acting as catalysts, (*b*) processes in which the wood is dissolved in concentrated acid, hydrolysis being effected on subsequent dilution. This latter classification has not yet received commercial application owing to the high cost of the acid and the expense and labour of recovery of the spent acid liquor. The French patent of Ekström[1] is of this type. Treatment with 95 per cent. sulphuric acid for twenty minutes followed by dilution to 1 per cent. acid strength and digestion for a period of one to five hours was specified for high conversion of cellulose to fermentable sugars.

In the dilute acid processes, Simonson[2] employed dilute sulphuric acid of 0·5 per cent. strength. A pressure of nine

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[1] F.P. 380358/1907.

[2] *Zeitsch. angew. Chem.*, 1898, 195, 219, 962, 1007.

atmospheres was employed, the material being in the proportions of one part of wood to four parts of the dilute acids. Digestion for a period of one-quarter of an hour was said to yield fermentable sugars sufficient to give a yield of alcohol equal to 6 per cent. of the dry wood employed.

In some recent modifications of the dilute acid process the operations have been directed towards the use of hydrochloric and sulphurous acids with a considerably smaller moisture content. The work of A. C. Classen directed attention more particularly to the use of sulphur dioxide as the hydrolytic agent, and its commercial development is being actively pursued. An acid concentration of 1 per cent. is employed. The moisture content is kept as low as possible for the sake of economy in the subsequent neutralisation and concentration processes, as well as for greater ease of regulation of the temperature—time factors which are of great importance for successful operations. It has been found that a 50 : 50 wood–acid liquor ratio is not above the saturation limit of the wood, which can therefore be handled in conveyors as with the original sawdust. The heating is effected by means of steam, the operating pressures being from 75–100 lb.

The separation of the sugars from the woody residue of the hydrolytic process is effected in standard beet-sugar diffusion batteries provided with suitable acid-proof linings. Neutralisation of the acid liquors is generally effected by means of lime, milk of lime, or a high grade limestone. The fermentation of the sugars is carried out in accordance with standard practice with a four-day fermentation period. (See Chap. XI.) The distillation and rectification of the alcohol are standard practice and involve no special problems. (Fig. 19.)

As to yields, obtained and possible, it may be observed that from 25 to 28 per cent. of the anhydrous wood may be rendered soluble, of which as much as 80 per cent. is fermentable sugar. Thus a yield of 20–22 per cent. of saccharoses corresponding with 10 to 11 per cent. of ethyl alcohol, equivalent to 35 gallons of 95 per cent. alcohol per dry ton of wood, represents the maximum goal. Actually, the average practical yields scarcely exceed half this amount, a figure of 20 gallons per dry ton being now good practice. Evidently there is a considerable margin for improvement.

The residue after the sugars are removed amounts to 70 per cent. of the original wood, and this also possesses a definite fuel value which may be utilised in the plant.

Thus far, the large-scale technical operations of the process have been confined to the United States, where, within the last ten years, according to a recent statement by Tomlinson,[1] two plants have been in continuous operation, producing a high-grade alcohol at costs comparing well with those of

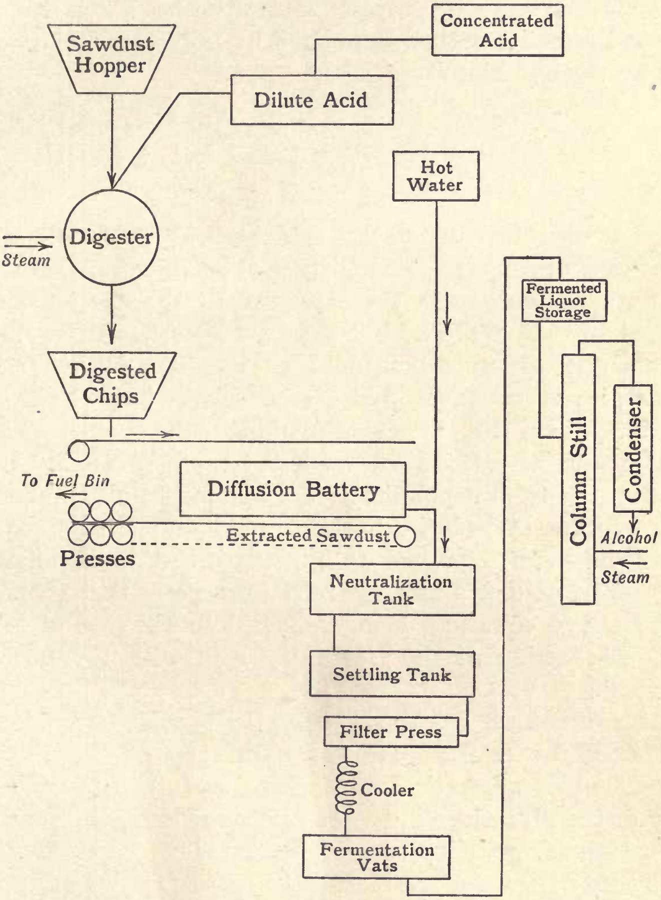

FIG. 19.

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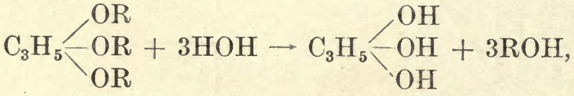
[1] Convention of Canadian Chemists, Ottawa, 1918.

other sources. It may be expected that similar developments will occur in Canada and other timber-producing areas.

The hydrolysis or saponification of oils and fats.—The principles of catalytic hydrolysis find extended industrial application in the hydrolysis of the glycerides in fats and oils for use in the soap, candle, and glycerine industries. The chemical reaction occurring in such hydrolysis may be generalised by the equation



$$C_3H_5\begin{cases}OR\\OR\\OR\end{cases} + 3HOH \rightarrow C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3ROH,$$

where R denotes any fatty acid radical. The reaction is a true case of a hydrolytic splitting of an ester into an alcohol and an acid, and, as in the cases previously treated, may be effected by water alone, but may be accelerated by the use of catalytic agents either acid or alkaline. When alkalies are employed to effect hydrolysis, conversion of the alkali and fatty acid to the corresponding salt occurs. This is, therefore, a true case of saponification. Actually in the industry the term saponification is applied to all the methods of promoting hydrolysis, both by acid and alkali, the term hydrolysis being confined to reports scientific in character. Whether by acid or alkali, the initial process is that generalised in the above equation, being followed in the case of alkalies by neutralisation of the free fatty acid with the formation of a soap.

The mechanism of the hydrolytic process may best be understood by reference to the hydrolysis of the glycerides of the simpler aliphatic acids, where, owing to the fair solubility of the glycerides in the catalytic medium, the conditions of operations are simpler and more readily controlled than is the case with the glycerides of the more complex fatty acids, which are but sparingly soluble, yield emulsions and insoluble, or only partly soluble, acids. Such study shows that the hydrolysis of the glycerides occurs in successive stages, di- and mono-glycerides being first formed as intermediate compounds yielding finally glycerine and the fatty acid. Thus Geitel[1] showed that the hydrolysis of triacetin, the

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[1] *J. pr. Chem.*, 1897, (ii), **55**, 417 ; 1898, **57**, 113.

glyceride of acetic acid, was apparently a monomolecular reaction, but that the velocities of hydrolysis of mono-, di-, and tri-acetates in dilute acids were in the ratios of 1 : 2 : 3. The parallel result with the acetates of glycol was demonstrated by Julius Meyer in 1907,[1] where the rates of hydrolysis of the two acetates were in the ratio of 1 : 2. Abel[2] and Kremann,[3] studying both acid and alkaline hydrolysis of esters of polyhydric alcohols, showed the same results as those of Geitel, and demonstrated that the apparent monomolecular nature of the hydrolysis of the complete glyceride was a mathematical consequence of the fact that hydrolysis occurred in the three successive stages, the rates of which were, as Geitel had shown, in the ratio of 3 : 2 : 1. Later work by Taylor[4] on neutral salt action in the acid hydrolysis of triacetin, further confirms this view.

It is without doubt true that the hydrolysis of the more complex glycerides in fats and oils obeys the same rule of successive stages of hydrolysis, modified naturally by the fact that the reaction occurs in a heterogeneous medium in which, as Lowenherz[5] showed, the velocity of reaction was constant and determined by the solubility of the ester in the catalytic medium. Instances in support of this view of successive stages as applied to the fats and oils may be cited. Lewkowitsch detected the presence of dierucin in an old sample of rape oil, and the observation of Gruen and Theimer[6] on the hydrolysis of distearochlorohydrin, in which the intermediate stages of the hydrolysis of the diglyceride were isolated, is decisive proof. Detection of intermediate compounds in partly saponified fats is, however, an extremely difficult matter.

Hydrolysis of fats and oils by water alone is perfectly possible, though, obviously, slow in practice. It was actually employed in practice in the process of R. A. Tilghmann, who caused the fat and water to be forced through a coiled pipe heated to 300°. The hydrolysis was incomplete, and destruction of the fatty matter occurred. In modern attempts to

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[1] *Zeitsch. Elektrochem.*, 1907, **13**, 186.

[2] *Zeitsch. physikal. Chem.*, 1906, **56**, 558.

[3] *Zeitsch. Elektrochem.*, 1907, **13**, 307.

[4] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, (*ii*), No. 34.

[5] *Zeitsch. physikal. Chem.*, 1894, **15**, 389.

[6] *Ber.*, 1907, **40**, 1801.

carry out hydrolysis by water alone, the use of superheated steam under pressures up to 15 atmospheres has been invoked, always, however, with the difficulty that the process is never complete.

The use of acids as catalysts has led to two distinct technical processes, the so-called Acid Process and the Twitchell Process. These may now be considered.

The acid process.—Lewkowitsch has shown that, using hydrochloric acid of sp. gr. 1·16 as catalyst, hydrolysis of fats and oils may be accelerated, but the process has not acquired technical importance as yet, since the reaction can be more readily accomplished using concentrated sulphuric acid as hydrolytic accelerator. At first sight this would appear to be an anomalous result in view of the known fact that hydrochloric acid is the stronger acid of the two. It is probably explained partly on the view that hydrochloric acid does not facilitate mutual solution of fat with water and on the fact that emulsification is small with hydrochloric acid as agent. Furthermore, sulphuric acid is probably effective through the formation of fatty sulphonic acids, which are doubtless stronger acids than the sulphuric acid itself, promoting also mutual solubility in the two phases and emulsification.

The action of sulphuric acid as hydrolytic agent was first described by Cornett in 1777. As now employed in practice, the operation is briefly somewhat as follows. The fat is first heated to 120° to free it from water and then run in the molten state into a mixing machine, in which it is thoroughly admixed with 4 to 6 per cent. of concentrated sulphuric acid of a gravity of 66° Bé. With acid of such strength, the subsequent hydrolytic change attains its maximum. During the process of mixing, which occupies twenty to thirty minutes, reaction is vigorous, the mass chars to a certain extent, and some reduction of sulphuric to sulphurous acid occurs. In this part of the process mixtures of sulphonated fatty acids, sulphuric esters of glycerol as well as the free acids, and various products of secondary reactions are undoubtedly present. After completion of this reaction, the mass is boiled with water, the free fatty acids rising to the surface and the glycerine remaining behind in the aqueous solution of sulphuric acid.

It is this second stage of the process which forms the real hydrolysis.

A considerable advantage in the employment of the acid process is the increase in the yield of solid fatty acids over that attained by other processes. This has been demonstrated by Lewkowitsch to be due to conversion of a portion of the oleic acid into the solid iso-oleic acid by a complex series of changes involving the intermediate formation of sulpho-oxy-stearic and oxy-stearic acids. This conversion is one of great technical importance, since it results in increased yields of candle material.[1] The glycerine yield is smaller than that obtained by catalytic processes employing alkalies.

The Twitchell process.—The importance of the catalytic agent employed, in the successful operation of a catalytic process, is beautifully demonstrated in the Twitchell process for the hydrolysis of fats and oils into glycerine and fatty acid. The Twitchell reagent also exemplifies excellently the applicability to practical problems of knowledge accumulated in the course of theoretical investigation. In this particular case, the theoretical knowledge did not precede the invention, since the first patent for the Twitchell process[2] was granted at a time when the attention devoted to catalytic processes was not so pronounced as it now is, and when the theoretical point of view relative to the mechanism of the process was by no means so developed as it is to-day.

In an investigation of the catalytic *rôle* of sulphuric acid in the hydrolytic splitting of fats and oils, Twitchell observed that sulphur compounds produced by the action of the sulphuric acid upon the fat might be separated from the fatty material by suitable methods of extraction, and could readily be identified as sulphonic acids. To such acids Twitchell attributed the catalytic properties observed in the Acid Process of hydrolysis. Accordingly, he prepared sulpho-acids of the fatty acids, such as sulpho-stearic acid, and such reagents were the agents first employed by him for the hydrolysis. Later, the accidental discovery of fatty aromatic sulphonic acids yielded the reagents which have been put

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[1] See Lewkowitsch, "Chem. Techn. Oils, Fats, and Waxes," Vol. 3, p. 188.

[2] U.S.P. 601603, July, 1897.

to practical use in the separation of glycerol and fatty acids. The original aromatic fatty sulphonic acid was made by treatment of a mixture of benzene and oleic acid with an excess of sulphuric acid. On pouring the mass into water, an oily layer of the desirable product resulted.[1] Instead of benzene, naphthalene is used with oleic acid in the manufacture of the commercial article, and other hydrocarbons may also find application. Such catalytic agents, when added in the proportion of half a per cent. or less to fat boiling with water in an open tank, will cause the separation of the glycerol.

The views of Twitchell in regard to the properties of a suitable catalyst for the hydrolysis of fats have been expressed in his paper, "A Reagent in the Chemistry of Fat." The catalyst should be a strong acid, highly dissociated in water, and should be soluble both in the fat to be hydrolysed and in the water. It should also tend to promote the solution of one in the other. It is now well known that the aromatic sulphonic acids are very strong acids, comparable in strength with strong mineral acids such as hydrochloric acid. The introduction of higher fatty radicals into the nucleus confers upon such acids the physical character of fats or oils, thereby increasing the mutual solubility, whilst at the same time yielding soapy solutions with water. The activity of the hydrolytic agent has been attributed to the emulsifying action of the reagent, promoting the formation of an intimate mixture of oil and water, thereby exposing a greater surface of action to the reagent. It must be observed that emulsification alone is not a sufficient explanation, as fats do not hydrolyse at 100° to any practical extent with water alone, even with good emulsification. It is to the presence of the strong acid and the promotion of mutual solubility as much as to emulsification that the efficient hydrolysis must be attributed.

The first operation in the process usually consists in the removal of foreign impurities by boiling the fatty material with dilute sulphuric acid. The fat is then transferred to open wooden tanks, and mixed with half its weight of water to which is added 2 per cent. of the catalytic agent. The mass is then thoroughly agitated by blowing through the

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[1] U.S.P. 628503, July, 1899.

system live steam from perforated coils in the tanks. Hydrolysis is complete in about an hour, after which the emulsion is destroyed by the addition of dilute sulphuric acid. Two layers separate, the fatty acid in the upper and the glycerine in the aqueous layer below.

The advantages to be gained by the use of the Twitchell process are many. In operation it is simple and the capital cost of plant required is low. It can also be employed in large units as contrasted with the small units and heavy initial cost of earlier hydrolytic processes. The process is operated at the ordinary pressure. The process of hydrolysis is practically complete and for low-grade fats it is especially suitable. In this way, materials such as garbage-grease and the footings of cotton-seed oil can be employed as raw materials in the soap or candle industry, thus releasing higher grade fats for use as food products. With low-grade materials, fractional distillation of the fatty acids is necessary to improve their purity and colour. The glycerine liquors obtained are free from salts, and so the process of concentration is much facilitated. Since the product of hydrolysis is the free fatty acid, the more economical sodium carbonate can be used in place of caustic liquor in the production of soaps.

The process is now extensively used, not only in America, but also in the continental European countries. The larger soap plants in Germany, Austria, Belgium, Holland, and Scandinavia operate principally with the Twitchell process. Its use in this country is increasing.

An analogous patent to the Twitchell patents has recently been obtained by Petroff in Russia. In this case the reagent employed is obtained as a by-product in the refining of petroleum with fuming sulphuric acid. The compound is a simple sulphonic acid of hydrocarbon radicals, probably not of the paraffin series. It is now being largely employed as an efficient catalyst for hydrolytic splitting.

Saponification of oils and fats by alkalies.—In considering the technical use of alkaline catalysts for promoting the hydrolysis of glycerides, the same general principles hold that were enunciated in the previous theoretical treatment. It will be shown that the rate of saponification is directly proportional to the effective concentration of the base employed, which also determines the time and temperature conditions to be observed for completion of the hydrolysis.

The technical processes concerned may be treated in two sections: (*a*) Saponification with the aid of alkaline earths, (*b*) saponification with the aid of caustic alkalies.

Saponification with lime and magnesia. The autoclave process.—Triglycerides may be saponified completely by solutions of lime in open vats at the boiling point, provided an excess of lime be used. The quantity of alkaline earth required amounts on the average to 12–14 per cent. by weight of the oil. This method of saponification was introduced into industry by de Milly in France. Live steam is used to heat up the material in lead-lined vats, and serves also to keep the mass in a state of agitation and of intimate mixture or emulsification. The calcium soap of the fatty acid is formed in the process, the glycerine remaining in the aqueous solution. Decomposition of the soap is effected with the aid of sulphuric acid, the fatty acid forming a floating layer on the liquid, the precipitated sulphate separating to the bottom.

The lime employed functions as a catalyst, and it is not necessary to use sufficient for complete conversion of the fatty acid to calcium salt. On the other hand, if smaller quantities of lime be used the concentration of catalyst, and therefore the catalytic activity, are diminished, so that other means must be employed to accelerate the reaction. This is done by carrying out the process in autoclaves under pressure. In such case, the temperature employed can be considerably increased beyond the boiling point of water, whereby the velocity of reaction is considerably augmented. Thus, with only 1 per cent. of lime under a pressure of 12 atmospheres, corresponding with a temperature of 190°, a virtually complete hydrolysis may be effected. It will be obvious that such a reduction in the quantity of lime employed is of considerable advantage in the economy of sulphuric acid required to decompose the calcium soap formed. In actual practice, it is customary to employ somewhat more lime than the above for the autoclave process, as the employment of high temperatures causes discoloration of the fatty acids produced. Modern practice in the candle industry calls for a working pressure of eight atmospheres with the addition of about

3 per cent. of lime. The process of hydrolysis is practically complete in about eight to ten hours. The reaction is rapid in the first two hours, as much as a 77 per cent. conversion being obtained. In the succeeding period, the percentage of hydrolysis slowly increases to a maximum of about 99 per cent. at the end of the tenth hour. For soap manufacture the hydrolysis must be conducted at still lower pressures in order to avoid discoloration. A pressure of 5 to 6 atmospheres is employed and the degree of hydrolysis reaches about 80 per cent.

Magnesia and zinc oxide have also been employed as catalytic accelerators. They have the advantage that they do not yield insoluble sulphates on treatment of the fatty soaps produced in the hydrolytic process. On the contrary, owing to their less basic character, the rate of hydrolysis is not so rapid and the percentage hydrolysed not so considerable. Magnesia also shows a tendency to produce emulsions not readily discharged in the subsequent treatment. Zinc oxide with the addition of zinc dust has been used together with lime in the ordinary autoclave process. The product, it appears, is less discoloured.

Saponification with caustic alkalies.—It is obvious that, owing to their solubility and the consequent high concentration of catalytic agent thereby attained, hydrolysis with caustic alkalies should be rapid and complete. Moreover, the temperature required is by no means so considerable as is required with alkaline earths. Hydrolysis of fats with caustic alkalies is the *metier* of the soap-maker. Sufficient of the hydrolytic agent is used to combine with all the free fatty acid formed to yield the sodium or potassium salts which constitute the basic material of the normal soaps of industry. Actually an excess of the alkali is always used to facilitate the hydrolytic process. There is no doubt, however, that the hydrolysis could be catalytically effected in the presence of only small amounts of such hydrolytic agents. A readjustment of time and temperature conditions would, however, be necessary.

Two processes of alkali saponification are employed in the preparation of soap, differentiated by the temperature at which the saponification is effected.

In the cold process, as the name implies, no external heat is applied. In consequence, a long period of saponification is necessary. The molten fat is churned up with the requisite quantity of alkali dissolved in water sufficient in amount to give to the soap the desired degree of hardness and solubility. Reaction sets in and the mass thickens. Sufficient heat of reaction is given out to bring about further saponification in the adjacent layers, with increasing velocity owing to rise of temperature, the oil assisting by preventing dissipation of the heat. This process continues throughout the mass and is complete in twenty-four to thirty-six hours, when about 97 per cent. of the glyceride has been converted into glycerine and soap. After the initial operation, the conversion is effected in frames, and when saponification is complete the mass is sufficiently solid that it may be cut into slabs. Obtained in this manner, the soaps always contain a small excess of free alkali, which for many purposes is an unsuitable ingredient.

Neutral soaps are obtained by means of the hot process. The hydrolysis is carried out in large soap kettles. The oil is brought to 80° by means of steam, which condenses to water in the system. Caustic soda is then gradually added to the contents of the pan, and ebullition is brought about by further introduction of live steam. In this process, also, the velocity of saponification is accelerated by the heat of reaction. The quantity of caustic alkali to be used is governed by the nature of the oil to be saponified, and, when addition is complete, the separation of the soap from the glycerine liquors is assisted by salting out with common salt. The subsequent operations in the hot process are concerned with the further refinement of the soap curd to ensure complete hydrolysis of the fats and a grading of the material obtained according to the soap value.

THE HYDROLYSIS OF ACYL DERIVATIVES

In addition to his studies on the hydrolysis of esters in presence of acids, Ostwald[1] investigated the hydrolysis of acetamide in order to determine the relative strengths of acids, arranging these in a table of decreasing activity from

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[1] *J. pr. Chem.*, 1883, **27**, 1.

hydrochloric to acetic acid. Since this early work, the process has frequently been employed in the endeavour to obtain a clearer comprehension of catalytic activity. As was shown by Crocker and Lowe,[1] the reaction is catalysed by both acids and bases, the hydrolysis proceeding in every case investigated as in ester hydrolysis, more rapidly with alkalies than with acids under similar experimental conditions. The rate of hydrolysis was shown to diminish in a homologous series with increasing complexity of amide. Aliphatic amides are more readily hydrolysed than aromatic amides, and the influence of substitution in the benzene ring is marked.[2] The reaction in both acid and alkaline solutions is bimolecular in accordance with the equations :

$$\begin{aligned} &(a)\ R\cdot CO\cdot NH_2 + H_2O + HX &&= R\cdot COOH + NH_4X, \\ &(b)\ R\cdot CO\cdot NH_2 + H_2O + MOH &&= R\cdot COOM + NH_4\cdot OH, \end{aligned}$$

Crocker and Lowe showed, however, that good reaction constants were obtained if, instead of the concentration of base and acid, the ionic concentrations were substituted.

Acree and Nirdlinger[3] drew the same conclusion, independently, in a study of the hydrolysis of various concentrations of aqueous acetamide, using different strength of hydrochloric acid, and suggested that it was a complex cation

$$\overset{+}{(CH_3\cdot CO\cdot NH_2\cdot H)}$$

which underwent hydrolysis. The ammonium chloride formed was shown to have a marked accelerating action on the hydrolysis. Added neutral salts acted similarly, the phenomenon being subsequently associated with the view that both ions and undissociated molecules may possess catalytic activity.[4]

The hydrolysis of amides of dibasic acids was investigated by von Peskow and Meyer,[5] and showed marked points of divergence from the results of Meyer with esters of dibasic acids. The values of the reaction constant obtained showed an initial

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[1] *J. Chem. Soc.*, 1907, **91**, 593, 952.

[2] Sudborough, *ibid.*, 1894, **65**, 1030 ; 1895, **67**, 587 ; 1897, **71**, 229.

[3] *Amer. Chem. J.*, 1907, **38**, 489.

[4] Acree, *ibid.*, 1912, **48**, 352 *et seq.*

[5] *Zeitsch. physikal. Chem.*, 1913, **82**, 129.

steady decrease with progress of hydrolysis, and only after some time yielded steady values. The abnormality is associated with the relative values of the velocities of hydrolysis of the two amide groupings. The researches on dibasic esters showed that an apparent unimolecular reaction constant was explainable on the assumption that the reaction constants of hydrolysis of the two groupings were in the ratio 2 : 1 (see p. 268). It was shown that with the amides in acid hydrolysis k_1 is smaller than k_2, whereas with alkalies, k_2 is the smaller. This was assumed to be connected with a repulsion between the negatively charged acid amide radical ($NH_2{\cdot}OC{\cdot}R{\cdot}CO{\cdot}O'$) and the negatively charged OH' grouping, whereas, in the acid reaction an attraction to the hydrogen ion would ensue.

HYDROLYSIS OF HALOGEN DERIVATIVES OF ORGANIC ACIDS

A well-investigated mechanism of hydrolytic acceleration is to be found in a study of the hydrolysis of halogen acetic acids and their sodium salts. The hydrolysis of chloroacetic acid by hot water proceeds quantitatively according to the equation :

$$CH_2Cl{\cdot}COOH + H_2O = CH_2{\cdot}OH{\cdot}COOH + HCl,$$

and the reaction is unimolecular,[1] even with wide variation of the initial acid concentration.[2] The reaction is not greatly affected by hydrogen chloride, formed or added, or by the addition of neutral salts such as sodium chloride in normal solution.

The hydrolysis of neutral sodium chloroacetate in dilute solution was shown by Senter to be unimolecular with slight deviations in normal solutions. The rate of reaction is diminished by certain neutral salts. In presence of alkali, the reaction is bimolecular in dilute solution, and may be formulated by the equation :

$$CH_2Cl{\cdot}COONa + NaOH = OH{\cdot}CH_2{\cdot}COONa + NaCl.$$

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[1] Schwab, Van't Hoff, "Studien zur Chemischen Dynamik."

[2] Senter, *J. Chem. Soc.*, 1907, **91**, 461.

This reaction, however, is accelerated by the addition of neutral salts, in marked contrast to the influence of such salts on the alkaline hydrolysis of esters. The accompanying table shows the effect of a series of neutral salts on the velocity of the hydrolytic processes occurring (*a*) in a solution of $N/10$-sodium bromoacetate and $N/10$-sodium hydroxide, (*b*) in a solution of $N/40$-ethyl acetate and $N/40$-sodium hydroxide.[1]

Neutral salt.	Increase per cent. of velocity coefficient in reaction (*a*).	Increase or decrease of velocity coefficient per cent. in (*b*).
$N/1$-Sodium nitrate	—	−19
,, chlorate	+51	−12
,, sulphate	—	+12
,, ferrocyanide.. ..	+53	0
,, benzenesulphonate	+51	—
,, benzoate	+51	−100
,, formate..	+100	+3
,, acetate	+102	0
,, tartrate..	+98	+8

A careful series of investigations of the great activity of neutral salts of organic acids in the former reaction as compared with that in alkaline ester hydrolysis showed that the activity was closely associated with the mechanism of the reaction. The effect was traced[2] to the intermediate formation of sodium acyl oxyacetates, as exemplified in the equation,

$$CH_2Br{\cdot}COONa + CH_3{\cdot}COONa = CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}COONa + NaBr,$$

which compounds are hydrolysed by alkali as fast as formed. In neutral solution, the compounds are hydrolysed slowly, and therefore set the tempo of the reaction and determine the influence of neutral salts in such solutions.

Senter and Ward, in connection with this work, investigated also the hydrolysis of acetoxyacetic acid and its salts in neutral, acid, and alkaline solutions. It was shown that the hydrolysis of the acid was catalysed by hydrogen ions either autocatalytically with ions from the acid itself or from added acids. The hydrolysis of the acid is ten times as rapid as that of the sodium salt under similar conditions, doubtless due to the absence of the accelerating hydrogen ions. In alkaline solution, the acceleration was enormous, the effect of $N/10$-sodium

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[1] Senter and Bulle, *J. Chem. Soc.*, 1912, **101**, 2528.

[2] *Loc. cit.*, and Senter and Ward, *J. Chem. Soc.*, 1912, **101**, 2534

hydroxide being to speed up the reaction to 100,000 times its velocity in aqueous solution. More recently, Holmberg[1] has studied this reaction in aqueous acid and alkaline solution, with similar results, in development of his researches on cation catalysis.

The hydrolytic decomposition of the bromo-substituted organic acids exhibits an interesting case of negative catalysis, the hydrobromic acid formed in the reaction retarding the velocity of reaction so that the constants calculated for a unimolecular reaction show a continuous decrease. Müller[2] formulated this anticatalytic effect of hydrobromic acid in the hydrolysis of bromosuccinic acid, assuming the reaction velocity to be proportional to the unchanged bromosuccinic acid and inversely to that of the hydrobromic acid formed, thus obtaining an equation of the form

$$\frac{dx}{dt} = k\frac{(a-x)}{(x)},$$

which gave satisfactory agreement with experimental results.

Senter[3] showed that, in the hydrolytic decomposition of bromopropionic acid, the reaction mechanism was not so simple as that assumed in the case of bromosuccinic acid. With the assumption that both the non-ionised acid and the $CH(CH_3)BrCOO'$ ions undergo change, each at their own definite reaction velocities, Senter and Porter[4] successfully interpreted the experimental results. The anticatalytic influence of the hydrobromic acid would on this view be due to the suppression of the ionisation of the bromopropionic acid, calculation showing that, in this particular case, the velocity constants of hydrolytic decomposition of ion and undissociated acid were $k = 0{\cdot}030$ and $k_2 = 0{\cdot}00053$ respectively.

THE DIAZOACETIC ESTER REACTION

It was shown by Curtius[5] in 1883 that the diazo-esters interacted with water with evolution of nitrogen and formation

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[1] *Zeitsch. physikal. Chem.*, 1913, **84**, 451.

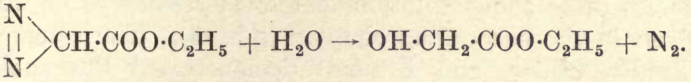
[2] *Ibid.*, 1902, **41**, 483.

[3] *J. Chem. Soc.*, 1909, **95**, 1836.

[4] *Ibid.*, 1911, **99**, 1049.

[5] *J. pr. Chem.*, (ii), 1883, **38**, 401.

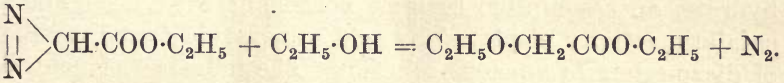
of hydroxy-derivatives of the ester residue as exemplified by the equation :



$$\begin{array}{c}N\\ \|\\ N\end{array}\!\!>CH\cdot COO\cdot C_2H_5 + H_2O \rightarrow OH\cdot CH_2\cdot COO\cdot C_2H_5 + N_2.$$

Bredig and Fraenkel[1] showed that the reaction was catalytically accelerated by the presence of acids and, by a study of the reaction velocity in the presence of a widely varied series of acids as well as with mixtures of acetic acid and sodium acetate, demonstrated a close proportionality between hydrogen-ion concentration and the rate of evolution of nitrogen. The extreme sensitivity of the reaction to hydrogen ions was made use of in a succeeding investigation of Spitalsky,[2] who determined with its aid the degree of hydrolysis of potassium dichromate. With this method it could be shown that, in a dilute solution containing 0·0169 mol. of the dichromate per litre, the hydrogen-ion concentration of the chromic acid produced by hydrolysis was 0·000098 mol. per litre. An even more striking application of the sensitivity of the reaction was made by Walker and Cumming,[3] who applied the diazo-method to the determination of the hydrion concentrations of amphoteric electrolytes, excellent experimental agreement being obtained between the values obtained and those calculated by Walker. Thus for a $N/32$-anthranilic acid solution, the found and calculated values were respectively $C_H =$ 0·000275 and 0·00027.

If the diazo-ester decomposition occur in alcoholic solution, the ester splits off nitrogen and adds on a molecule of alcohol, which change may be represented by the equation :



$$\begin{array}{c}N\\ \|\\ N\end{array}\!\!>CH\cdot COO\cdot C_2H_5 + C_2H_5\cdot OH = C_2H_5O\cdot CH_2\cdot COO\cdot C_2H_5 + N_2.$$

This reaction is also markedly sensitive to the presence of hydrogen ions, and can be used, likewise, for the determination of hydrion concentration in alcoholic solutions. In working out the process, Bredig and Fraenkel[4] noted the retarding

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[1] *Zeitsch. physikal. Chem.*, 1907, **60**, 202.

[2] *Zeitsch. anorg. Chem.*, 1907, **54**, 265.

[3] *Zeitsch. physikal. Chem.*, 1907, **57**, 578.

[4] *Loc. cit.*

influence of small quantities of water on the reaction velocity, in many aspects similar to that observable in esterification processes in alcoholic solution, extended treatment of which is given in the succeeding chapter (p. 295). The researches of Bredig, Millar, and Braune[1] demonstrated the analogy between the results in the two reactions, even to numerical agreement in the calculations of the hydrolytic constant of the hydrogen-ion alcoholate assumed by Goldschmidt to be the active catalytic agent (*vide* p. 298). Millar was able to show, not only that addition of water decreased the velocity of decomposition in alcoholic solution, but also that alcohol decreased the velocity of decomposition in aqueous solution. The appended table illustrates this fact with a picric acid concentration of 0·000909 mol. per litre as catalyst in each solvent medium.

Grams alcohol per 100 grams of reaction mixture.	k_{25}	Mols. of water per litre.	k_{25}
0	0·0356	0	0·057
3·31	0·0320	0·16	0·033
6·69	0·0289	0·64	0·018
14·2	0·0204	2·56	0·0064
21·9	0·0133	5·12	0·0044
		10·24	0·0049
		15·36	0·0070

The minimum value for k occurs at a concentration of 6 mols. of water per litre, or at a water concentration of 11 per cent. This anticatalytic effect of each on the other is extremely interesting and important in respect of the theoretical interpretation. Goldschmidt's esterification hypothesis seems scarcely applicable, without modification, to the present case, since it assumes non-activity of the free ion and ion-hydrate, an assumption scarcely consonant with the marked catalytic activity displayed by acid catalysts in decomposition of diazo-esters in aqueous solution. The influence of neutral salts with a common anion on the catalytic activity of the acids was studied by Snethlage,[2] who showed that the experimental results obtained were in harmony with the theory that the undissociated molecule of the catalysing acid possessed catalytic activity.

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[1] *Zeitsch. physikal. Chem.*, 1913, 85, 129, 170.

[2] *Ibid.*, 1913, 85, 238.

CHAPTER IX

DEHYDRATION

THE removal of the elements of water from a compound or compounds with simultaneous production of a new substance is one of the earliest types of reaction studied from the catalytic point of view. The dehydration of alcohol by means of sulphuric acid, yielding ether or ethylene, forms one of the classical examples of reaction in homogeneous liquid systems from the theoretical point of view, whilst possessing a technical importance no less great in the processes of organic synthesis. There will be shown in the succeeding pages the wide applicability of catalytic dehydration processes operated both in homogeneous and in heterogeneous systems. The reactions comprise the production of ethers and hydrocarbons by dehydration of alcohols, the production of esters by removal of the elements of water from an alcohol and an acid, as well as processes of dehydration in which are produced compounds as varied as aldehydes, ketones, lactones, anhydrides, amides, thiols, and many others.

ETHERIFICATION AND HYDROCARBON FORMATION

Dehydration of alcohols.—The production of ether from alcohol and sulphuric acid at 140° is an example frequently cited in evidence of the fact that a small quantity of the catalytic substance is capable of accelerating the transformation of considerable quantities of the reacting substances. Further, the explanation of the mechanism of the process by Williamson in 1854, based upon the intermediate formation of ethyl sulphuric acid, is at once a classical and splendid example of the *rôle* of the intermediate compounds in many catalytic processes. It is demonstrable that alcohol and concentrated sulphuric acid may react together to yield an acid ester, ethyl sulphuric acid, and water, according to the interaction,

$$C_2H_5{\cdot}OH + H_2SO_4 \rightleftharpoons C_2H_5O{\cdot}SO_3H + H_2O,$$

the products being stable in the cold in presence of excess of alcohol. At 140°, however, the ethyl sulphuric acid is capable of combining with further quantities of alcohol to produce ethyl ether with the simultaneous regeneration of sulphuric acid as follows :

$$C_2H_5O{\cdot}SO_3H + C_2H_5{\cdot}OH \rightleftharpoons (C_2H_5)_2O + H_2SO_4.$$

If the whole process be conducted, *ab initio*, at 140°, ether distils off uninterruptedly if alcohol be supplied continuously to the system, and theoretically the process might continue indefinitely. Actually, in practice, dilution of the acid with water and its partial reduction to the lower state of oxidation by side reactions cause the process of etherification finally to cease.

Ethyl sulphuric acid is capable of decomposing at higher temperatures into ethylene and sulphuric acid, which latter may again react with alcohol and yield further quantities of ethylene :

$$C_2H_5O{\cdot}SO_3H \rightarrow C_2H_4 + H_2SO_4.$$

This, therefore, is a parallel catalytic process to the above, and predominates at temperatures of 160–170°, though naturally it must occur to some extent at the lower temperature of etherification. It will be obvious also that the attainment of successful yields in the production of ether is dependent to a degree on the avoidance of the secondary reaction yielding ethylene.

The production of ether on the technical scale is one of considerable importance, since ether functions as a solvent in many technical processes, more especially those connected with the manufacture of explosives and the organic chemical industry. Some details of the process as operated may therefore be given.

The original types of plant were adaptations of the laboratory methods of preparation to the condition of technical operation. Definite mixtures of alcohol and sulphuric acid were distilled from suitable containers and the disappearance of alcohol by conversion into the reaction products was compensated for by continuous addition. The distillate subsequently underwent processes of purification whereby the secondary products of reaction were removed, the final rectification being a process of fractional distillation. The process as thus conducted was cumbersome in detail, and ill-designed to meet the recent requirements for large output. Such plant, therefore, has given place to designs more adapted to the needs of the various industries concerned. Actually, in the reorganisation, the type of catalytic reaction has been changed from a reaction in homogeneous liquid system to one between alcohol vapour and the liquid catalytic agent, sulphuric acid of a definite concentration maintained at a fixed temperature in the neighbourhood of 140°. The alcohol is vaporised in a series of preheaters and passes thence directly into the catalyst medium. Reaction occurs with evolution of heat, so that it is necessary to cool the sulphuric acid by means of tubes immersed in the liquid through which cold water is flowing. The products of reaction, ether and water, together with a certain quantity of unchanged alcohol, pass away from the catalyst in the form of vapour directly to a dephlegmator in which the constituents of the mixture are fractionally condensed. At the lowest exit from the fractionating column, the water is removed. At a higher level, pure alcohol is drawn off and returns to the incoming system, whilst at the highest point in the system the ether is condensed and removed. Owing to the fact that the ether vapour travels before final condensation through the vapour of absolute alcohol, the ether obtained is very efficiently dehydrated. Ether of the highest grade of purity is thus obtained in a one-stage continuous operation. The product is so pure that it has been stated to be better than that obtainable in the laboratory with the best refinements of working. The over-all yield of the process in ether is practically quantitative, a trustworthy figure quoting more than 97 per cent. conversion of alcohol to ether. The percentage of the inflowing alcohol converted in one operation amounts to 75, the residue flowing back, as mentioned, from the fractionating column to the inflowing alcohol. In the operation of the improved system, side reactions are practically completely eliminated, whilst, since the water is removed in the resultant vapour phase, dilution of the catalytic medium is obviated.

As catalytic agent, various acids other than sulphuric have been suggested and employed. Phosphoric acid has found use in this manner, as it is more difficultly reduced than sulphuric acid and so may have a longer period of activity. Similarly, a recent process of Kraft employs benzenesulphonic acid for the preparation of ethyl ether and other members of the series, and other aromatic sulphonic acids may be employed in like manner. However, it may safely be stated that their use is unnecessary in the light of the information recorded above as to operation with sulphuric acid.

For the synthesis of more complex ethers the method of catalytic dehydration of the corresponding alcohols is in general unsuitable. It is found that at the temperatures necessary to effect dehydration to ether, the complete dehydration to hydrocarbon also occurs to a marked degree. Thus, even with propyl alcohol a considerable amount of propylene is formed simultaneously with the ether, the yield of which, therefore, is correspondingly reduced. The predominance of hydrocarbon formation is still more marked in the case of secondary and tertiary alcohols.

A variety of other catalytic materials has been employed to effect the dehydration of alcohols. A clue to the nature of suitable agencies for such operations is at hand in the well-known practice of adding sand to the sulphuric acid–alcohol mixture, employed for the preparation of ethylene, in order to ensure a steady gentle evolution of the gas. Grigorieff[1] first indicated the use of alumina as a dehydrating agent for alcohols. Extended investigation of such catalytic agents, principally by Sabatier and Mailhe,[2] has shown that

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[1] *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 173; *Bull. Soc. chim.*, Paris, 1902, (iii), **26**, 612.

[2] *Ann. Chim. Phys.*, 1910, (viii), **20**, 289.

carbon, phosphorus, and a number of oxides as well as solid dehydrating agents such as zinc chloride, basic aluminium sulphate, and anhydrous calcium sulphate, all promote the dehydration of alcohols.

In the main, the elimination of water produces the corresponding hydrocarbon. Only with alumina at 210° has the production of ethyl ether been noted. At more elevated temperatures, production of ethylene is practically quantitative. Baskerville[1] failed to get ether from alcohol, using thoria as agent, even at temperatures as low as 250°. With phenols, however, in presence of thoria at 400–500°, aromatic oxides result:

$$2C_6H_5{\cdot}OH = (C_6H_5)_2O + H_2O,$$

and simultaneous dehydration of a phenol and alcohol, using thoria at a temperature of 400°, gives a mixed aliphatic aromatic ether:

$$C_6H_5{\cdot}OH + C_2H_5{\cdot}OH \rightarrow C_6H_5{\cdot}O{\cdot}C_2H_5 + H_2O.$$

Animal charcoal is, when compared with certain metallic oxides, a relatively poor dehydrating catalytic agent. It is markedly inferior even to red phosphorus, which possesses quite active catalytic influence, with, however, the disadvantage that small quantities of phosphoretted hydrogen are simultaneously produced and must be removed from the resulting gaseous products.

Sabatier and Mailhe[2] investigated the activity of oxide catalysts at temperatures in the neighbourhood of 300–400°. It was shown that the majority of oxides promote two reactions simultaneously, one the process of dehydration, the other the process of dehydrogenation. By analysis of the gaseous products resulting from the dehydration of ethyl alcohol, it was possible to show that with certain catalysts ethylene was exclusively produced, but that, generally, it was admixed with a certain proportion of hydrogen. The following table shows a series of oxides arranged in the order of activity as dehydrating agents, the figures referring to the percentage of ethylene in the ethylene–hydrogen mixture produced by

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[1] *J. Amer. Chem. Soc.*, 1913, **35**, 93.

[2] *Loc. cit.*

passage of alcohol vapour over the oxide mass maintained at 340°–350°.

	Per cent.	
ThO_2	100	Dehydrating agents.
Al_2O_3	98·5	
W_2O_3	98·5	
Cr_2O_3	91	Mixed dehydration and dehydrogenation.
SiO_2	84	
TiO_2	63	
BeO	45	
ZrO_2	45	
U_3O_8	24	
Mo_2O_5	23	
Fe_2O_3	14	
V_2O_3	9	
ZnO	5	
MnO_2	0	Dehydrogenation agents.
SnO	0	
CdO	0	
Mn_3O_4	0	
MgO	0	
Cu	0	
Ni	0	

The figures indicate that thoria is exclusively a dehydrating agent under the conditions named, whilst alumina and the blue oxide of tungsten are practically quantitative in this respect. With the remainder, however, the dehydrogenation process more and more predominates until finally with oxides like SnO and CdO the dehydrating action is entirely suppressed.

Of the three effective agents, thoria is the most robust. Its activity decreases but slowly, and may readily be restored by ignition to redness. The blue oxide of tungsten is prepared *in situ* by reduction of tungsten oxide, and may be rejuvenated by reoxidation and subsequent reduction. Alumina is very sensitive as dehydrating agent to the physical state of the catalyst. The most active form is prepared by dehydration of the washed precipitated hydroxide (obtained by the decomposition of sodium aluminate with sulphuric acid) at a temperature of 300°. Ignition at higher temperatures renders the catalyst considerably less active. On the contrary, the active material prepared at 300° is very sensitive to accumulations of decomposition products in the catalyst mass, and its reactivity rapidly diminishes on this account.

The reversibility of the dehydration process in presence of these oxide catalysts is demonstrated by the recent researches of Engelder.[1] It was shown that the alcohol–water–ethylene equilibrium could be displaced with the oxides Al_2O_3, SiO_2, ZrO_2, and TiO_2, by addition of water vapour to the incoming alcohol. The result may not be without importance from the technical point of view, since it suggests a method of preparation of synthetic alcohol where convenient supplies of ethylene are available.

As is disclosed by the patent literature, the preparation of compounds containing conjugated double bonds by dehydration of aldehydes has been a matter of considerable importance in view of the possible condensation of these reactive products to terpenes and rubbers. Aluminium silicate at 500–600° is stated to be an effective dehydrating agent for this purpose. Thus, U.S.P. 1033327/1912 claims the use of this material for the dehydration of butyraldehyde and valeraldehyde, *e.g.*,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \rightarrow CH_2{:}CH{\cdot}CH{:}CH_2.$$

HOMOGENEOUS ESTERIFICATION

The elimination of the elements of water, from an alcohol and an acid jointly, gives rise to the formation of compounds known as esters, and the process itself is termed esterification. The reaction occurring may be generalised in the case of monobasic carboxylic acids by the equation :

$$R{\cdot}COOH + R_1{\cdot}OH = R{\cdot}COOR_1 + H_2O,$$

and, in a similar manner, reactions between polybasic carboxylic and other acids may be generalised.

The reaction occurring, as was shown in the classical studies of Berthelot and Paen de St. Giles as early as 1862, is a beautiful example of the reversible or balanced action. It is definable as to the equilibrium position by means of the Guldberg-Waage law of mass action formulated in 1867, and therefore subsequent to the actual experimental proof furnished by the studies on esterification. The researches of Berthelot and St. Giles demonstrated that, with equivalent initial concentrations of acetic acid and ethyl alcohol, for example, there was present at equilibrium one-third of the original concentra-

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[1] *J. Physical Chem.*, **1917**, **21**, **676.**

tions of acid and alcohol, and two-thirds of ester and water. According to the mass action law therefore,

$$K = \frac{C_{\text{acid}} C_{\text{alcohol}}}{C_{\text{ester}} C_{\text{water}}} = \frac{0{\cdot}33 \times 0{\cdot}33}{0{\cdot}66 \times 0{\cdot}66} = \frac{1}{4}.$$

It was further demonstrated that with varying proportions of alcohol this mass action constant was maintained, and that, therefore, in presence of excess of alcohol a high percentage of acid could be transformed to ester.

It was pointed out in the preceding chapter that the reverse action in this process, the hydrolysis of an ester, is catalytically accelerated by the addition or presence of numerous substances, and chief among such accelerating agents were acids. As is therefore to be expected, acids are also catalytic agents in the production of esters and have been consistently so used in preparative organic chemistry. Since acids behave as catalytic agents, it is obvious that the reaction between an alcohol and an acid is an auto-catalytic process, the acid undergoing esterification being itself a promoter of the reaction. In general, however, and especially in the esterification of weak acids, as, for example, acetic acid, addition of a strong acid catalytic agent is employed. Formerly, the principal acid catalyst was sulphuric acid, and it is still occasionally made use of as a convenient agent. Frequently, however, owing to its strong dehydrating and charring action, its use is impossible. In agreement with the observations made in the section on hydrolysis, the strong acid, hydrochloric acid, is, however, the better agent, and use of this acid is the basis of the modern method of esterification as worked out by Emil Fischer and Speier.[1] The method employed by them consists in heating the acid to be esterified with an excess of alcohol containing about 3 per cent. of dry hydrogen chloride dissolved in it as catalytic agent. After a period of time, dependent on several factors to be more fully discussed later, equilibrium is attained and the ester may be obtained therefrom in several ways. By raising the temperature to the boiling point of the mixture, the velocity of reaction is greatly accelerated. An earlier method employed by v. Meyer and Sudborough[2] was operated at the ordinary temperature,

[1] *Ber.*, 1895, **28**, 3252.

[2] *Ibid.*, 1894, **27**, 510.

compensation for the relative slowness of the reaction being effected by using saturated solutions of hydrogen chloride in the alcohol.

The more recent researches of Senderens and Aboulenc[1] demonstrate, however, that sulphuric acid can operate in a similar manner to hydrochloric acid. It was shown that on distillation of equimolecular proportions of acetic acid and ethyl alcohol 17·8 per cent. of the theoretical amount of ethyl acetate was formed. With 1 per cent. of sulphuric acid by volume, however, the yield is 86·5 per cent. of theory. The general applicability of this method was demonstrated in later papers.[2] Anhydrous aluminium sulphate and potassium hydrogen sulphate were also shown to be effective catalytic agents, 82 per cent. yields being obtained. Anhydrous sodium sulphate was without action, however, showing that the activity is not entirely due to the dehydrating action. This latter was emphasised by Kurtenacker and Habermann,[3] who also studied various other salts. A German patent[4] combines both dehydrating and catalytic activity in a proposal to produce ester quantitatively from alcohol and acid by boiling the components in presence of anhydrous calcium chloride and a mineral acid.

The velocity of esterification is sufficiently slow for convenient study, the progress of reaction being readily determined by the diminishing acid content of the system, due to the production of ester. As in the case of hydrolysis, therefore, the process of esterification has been the object of considerable study with a view to the elucidation of the theoretical aspects of the catalytic process.

The relationship between chemical constitution of acid and alcohol and the esterification process has occasioned considerable research. The work of Menschutkin[5] on the autocatalytic esterification of fatty acids demonstrated that the velocity of esterification diminished with increasing complexity of the acid and of the alcohol; it was more rapid, however, in the case of primary alcohols than with secondary

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[1] *Compt. rend.*, 1911, **152**, 1671.

[2] For example, *Compt. rend.*, 1913, **156**, 1620.

[3] *J. pr. Chem.*, 1911, (ii), **83**, 541.

[4] D.R.P. 232818.

[5] *J. pr. Chem.*, 1881, (ii), **24**, 49; 1882, (ii), **25**, 193; *Ber.*, 1897, **30**, 2783.

or tertiary alcohols. Side-chains, negative substituents, and unsaturated linkages in a primary alcohol also caused diminution of esterification velocity. These latter conclusions were supported by the subsequent determinations of Michael and Wohlgast[1] on the esterification of trichloroacetic acid by various alcohols. Exceptions to Menschutkin's observations are, however, noted by Lichty[2] in the case of chlorinated fatty acids, introduction of a chlorine grouping accelerating the velocity of esterification over that of the simple acid.

Parallel experiments on constitutive influence in the case of esterification in presence of hydrogen chloride as catalyst were first undertaken by v. Meyer, alone and in conjunction with Sudborough.[3] It was shown for example, that diortho-substituted benzoic acids were very resistant to esterification, the degree of inhibition being governed to a certain degree, however, by the nature of the substituent. Thus the influence of hydroxyl and methyl substitution was not so marked as that of nitro-, halide and carboxylic radicals. Substitution in other than the ortho-position had comparatively little inhibitory effect on the Fischer-Speier esterification method. The literature of this type of investigation has been multiplied enormously by the organic chemist with a view to the determination of constitutive influence, more especially as to the operation of steric hindrances.[4]

The researches of Goldschmidt and his pupils into the problem of esterification have been carried out with a somewhat different object, employing dilute alcoholic solutions of the acid to be esterified and using hydrogen chloride and other acids as catalyst. In such circumstances, the concentration of alcohol can be regarded as constant and the reaction velocity as interpretable by means of the monomolecular equation

$$K = \frac{1}{t} \log \frac{a}{a-x}.$$

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[1] *Ber.*, 1909, **42**, 3157.

[2] *Amer. Chem. J.*, 1895, **17**, 27; 1896, **18**, 590.

[3] *Ber.*, 1894, **27**, 510, 1580, 3146; 1895, **28**, 182. 1254.

[4] See, especially, Sudborough and his co-workers *J. Chem. Soc.*, 1898, **73**, 81; 1905, **87**, 1840; 1907, **91**, 1033; 1909, **95**, 315, 975; Wegscheider, *Monatsh.*, 1895, **16**, 75; 1897, **18**, 418, 629; 1899, **20**, 685; 1900, **21**, 621, 638, 787; 1902, **23**, 317, 357, 369, 393, 405, 1093; 1903, **24**, 413, 915; 1905, **26**, 1039; 1906, **27**, 487, 777; 1907, **28**, 819; 1908, **29**, 525, 531, 535, 541, 557; 1910, **31**, 1253.

Operating in this manner, it was shown that, as a rough approximation, the reaction constant varied proportionately to the hydrogen-ion concentration, and that the activity of different acid catalytic agents was in direct relation to the strength of the acid as determined by the hydrogen-ion concentration from conductivity data in alcoholic solution. Thus, in order of diminishing catalytic activity, came hydrochloric, picric, trichloroacetic, trinitrobenzoic, trichlorobutyric and dichloroacetic acids. Goldschmidt further showed that the ratio of the velocities of esterification of an organic acid with two different catalysing acids was constant and independent of the particular acid esterified in a given alcoholic solution. Thus, as the following table reveals, the ratio of the velocities of esterification, using hydrochloric and picric acids, averaged 13·5 with acetic, propionic, *n*-butyric, and phenyl acetic acid.

Acid.	k_a : *N*/10-HCl	k_b : *N*/10-Picric acid.	k_a/k_b.
Acetic	2·179	0·162	13·5
Propionic	1·544	0·115	13·1
n-Butyric	0·764	0·0582	13·1
Phenyl acetic	0·902	0·0655	13·8

With hydrochloric and sulphosalicylic acids as catalytic agents, the ratio was similarly constant.

Observation of the retardation of reaction velocity due to the influence of small quantities of water produced during the process of esterification or added to the reaction medium[1] led Goldschmidt[2] to the hypothesis that the active catalytic agent of the esterification process was an alcoholate

$$(C_2H_5{\cdot}OH{\cdot}\dot{H})$$

of the hydrogen ion of the catalysing acid. This alcoholate was regarded as interacting with the acid to be esterified, yielding the ester product. The retarding action of water was ascribed to reduction of the concentration of the active alcohol by hydrolysis to yield a non-active ion hydrate :

$$(C_2H_5{\cdot}OH{\cdot}\dot{H}) + H_2O \rightleftharpoons C_2H_5{\cdot}OH + (H{\cdot}OH{\cdot}\dot{H}).$$

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[1] Goldschmidt, *Ber.*, 1895, **28**, 3218 ; with Sunde, *ibid.*, 1906, **39**, 711 ; Kailan, *Monatsh.*, 1907, **28**, 115, 559 *et seq.* ; 1908, **29**, 799.

[2] *Zeitsch. Elektrochem.*, 1906, **12**, 432.

Thus if ζ = the equilibrium concentration of the ion alcoholate.
n = the initial concentration of added water,
x = the concentration of acid esterified and therefore of water formed in the reaction,
r = the equilibrium or hydrolytic constant of the above hydrolysis,
y = the equilibrium constant of ion-hydrate,

there follows, according to the mass-action law,

$$C_{C_2H_5\cdot OH\cdot \dot{H}} x C_{H_2O} = r . C_{C_2H_5\cdot OH} x C_{HO\cdot H\cdot \dot{H}}$$

or
$$\zeta(n + x - y) = ry \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In presence of excess of alcohol, which may therefore be regarded as constant, a simplified treatment of the problem may be obtained if assumption be made that y, the concentration of ion-hydrate, may be neglected in comparison with $(n + x)$, the total quantity of water present. In such cases equation (1) becomes

$$\zeta(n + x) = r . y \text{ or } y = \frac{\zeta(n + x)}{r} \quad . \quad . \quad . \quad (2)$$

the term r including the alcohol concentration term, assumed constant.

If ζ_0 represent the ion-alcoholate concentration in total absence of water, it follows that

$$\zeta_0 - \zeta = y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

ζ_0 may be expressed by application of the mass-action law to the equation

$$C_2H_5\cdot OH + \dot{H} \rightleftarrows (C_2H_5\cdot OH\cdot \dot{H})$$

in terms of c, the $\dot{H}$ ion concentration in absolute alcohol, the concentration of alcohol in mols. per litre (b), and ϕ the equilibrium constant of this reaction.

Thus $$\phi . c . b . = \zeta_0.$$

Substituting this value in (3), we obtain the values of ζ or y in terms of these magnitudes, viz.,

$$\zeta = \phi bc - y$$
$$y = \phi bc - \zeta$$

whence from equation (2)

$$\zeta = \frac{\phi bc . r}{n + x + r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now the velocity with which esterification occurs is proportional at any moment to the amount of unesterified acid and to the concentration of the catalyst, ζ. That is,

$$\frac{dx}{dt} = k(a - x)\zeta,$$

where a is the original concentration of the acid undergoing esterification. Substituting the value for ζ obtained in (4), there results

$$\frac{dx}{dt} = k(a - x)\ \frac{\phi bc\ .\ r}{n + x + r}$$

and this on integration gives the result

$$k\ .\ c\ .\ t\ . = n + r + a \log \frac{a}{a - x} - x \quad .\quad .\quad .\quad (5)$$

By determining two values of x at times t_1 and t_2, we obtain thereby with equation (5) two equations from which the value of r may be calculated. In this way Goldschmidt calculated a value for the hydrolytic constant $r = 0{\cdot}15$ at 25°, for hydrochloric and sulphosalicylic acids, the value varying but little with a whole series of different acids esterified in ethyl alcohol solution. At 0°, the value of r becomes 0·095.

The falling constant, K, obtained by application of the ordinary monomolecular equation and caused by the inhibiting influence of the water formed in the reaction, was to a marked degree corrected for by use of equation (5). Application of a still more exact, but also more complicated, formula obtained without neglecting the concentration of the ion hydrate y, as compared with $n + x$, gave even better concordance in the reaction constants.

The problem of retardation by traces of water has also been the subject of investigation by Lapworth and his co-workers. Lapworth and Fitzgerald[1] emphasised the point of view that the water acted by reducing the concentration of the free hydrogen ions present in the alcoholic solution by a simple process of hydration. Contrary to the Goldschmidt view point, the free hydrogen ion and not the alcoholate is assumed active; the ion hydrate, as with Goldschmidt, is regarded

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[1] *J. Chem. Soc.*, 1908, **93**, 2167.

as inactive. In a subsequent paper,[1] Lapworth directed attention to a number of reactions in which the anti-catalytic effect of water was marked, and proceeded to a mathematical development of the view put forward in the earlier paper. The addition of water to a dilute solution of hydrogen chloride in alcohol was regarded as the addition of a relatively strong base to a solution of an acid in a weak base. On this assumption, and making allowance for the removal of the catalytically active hydrogen ions by both water and alcohol as ion hydrate and ion alcoholate, Lapworth deduced for the velocity of esterification the equation

$$\frac{-du}{dt} = AK_2pxM' \frac{M}{\frac{K_2}{K'_2}M' + M},$$

where u is the active mass of the carboxylic acid,

p = a constant dependent on the nature of this acid,
M and K_2 refer to the active mass of water and equilibrium constant of the ion–ion hydrate equilibrium,
M' and K'_2 the corresponding magnitudes for alcohol,
x is the measured degree of dissociation, and A the total mass of the catalysing acid.

This is in accordance with the observations of Goldschmidt and Udby and with the equation previously deduced (p. 295).

$$\frac{du}{dt} = k(a-x)\frac{\phi bc\,.\,r\,.}{n+x+r},$$

as will be evident from the following comparison of symbols :

(G.)	$k\phi$	b	r	c	$a-x$	$n+x$
(L.)	$\frac{pK'_2}{M'}$	M'	$\frac{K_2}{K'_2}M'$	Ax	u	$M.$

The interpretations of the two equations, however, are by no means identical, for whereas Goldschmidt assumes that the ion alcoholate is the active catalytic agent in order to derive his equation, Lapworth assumes that the velocity of esterification is at any time proportional to the active masses of the carboxylic acid, the alcohol, and the free hydrogen ions.

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[1] *J. Chem. Soc.*, 1908, **93**, 2187.

To test further the idea of the availability or salt-forming power of an acid in various solvents on addition of a base relatively stronger than the solvent, preliminary tintometric determinations were made in alcoholic solutions of hydrogen chloride and in benzene and carbon tetrachloride solutions of trichloroacetic acid, using various bases and aminoazobenzene as indicator. Concordant values were obtained for the relative basic affinities in decreasing order of a series of weak bases, the order being carbamide, water, ether, ethyl alcohol, acetone, ethyl acetate, and methyl alcohol.

A more recent publication[1] deals more particularly with the "availability" of hydrogen chloride in alcoholic solution and the influence of water thereon. In this publication the availability of the acid is defined as a function proportional to its capacity for forming complex hydrions with any mono-acid base, which, mathematically expressed, becomes

$$P = \frac{\xi}{kB},$$

where P is the availability, ξ the concentration of complex ions, and B the concentration of free base, k the constant for the base used. By tintometric and esterification experiments the availability of a very dilute solution of hydrogen chloride in moist alcohol was shown to be nearly an inverse linear function of the amount of water present for quantities of the latter not exceeding a concentration of 0·5 mol. per litre. The availability in this range could be represented by an expression

$$\begin{array}{c} c\,.\,k \\ r + w \end{array}$$

where c = concentration of hydrogen chloride,
k = a constant,
w = concentration of water,
r = the water equivalent of the alcohol present, constant as was shown by Goldschmidt and Udby for a given alcohol, but within experimental error the same by measurements either of esterification or by determination of the salt formed with a weak mono-acid base.

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[1] Lapworth and Partington, *J. Chem. Soc.*, 1910, **97**, 19.

Interesting in regard to this latter conclusion of Lapworth and Partington is the conclusion reached by Bredig, Millar, and Braune that *r* (the water equivalent or basic water value of Lapworth and Partington ; the hydrolytic constant of Goldschmidt) was numerically the same in diazoacetic ester decomposition in aqueous alcoholic solution as in esterification measurements. This identity naturally suggests a common cause in each case, and, moreover, is of importance in a decision of the relative merits of the two points of view. For, as was pointed out in the preceding chapter in reference to diazo-ester decomposition, the Goldschmidt assumption of non-activity of the ion hydrate leaves only the hydrogen ion as the catalytic agent for the decomposition of diazo-ester in *aqueous* solution, and yet, in esterification, Goldschmidt's theory assumes both free ion and ion hydrate to be inactive, but the ion-alcoholate, however, to be active. In Lapworth's view, the free ion is the active agent, and is determined by the availability of the acid. Obviously, therefore, Lapworth's theory is applicable without modification to all the various acid catalytic processes here considered, whilst Goldschmidt's view requires adjustment to meet particular cases.

Lapworth and Jones[1] have extended the investigations to studies of the influence of temperature on the basic water value, *r*, of the theory and also to measurements of vapour pressures of hydrogen chloride in moist alcoholic solutions in order to obtain further evidence on the point of view put forward. It was shown both by the tintometric and by the esterification method that the value of *r* steadily increased with temperature from a value of 50×10^{-3} at 0° to 97×10^{-3} at 25°, in quantitative agreement with the results of Goldschmidt and Udby, who, however, employed a different concentration of catalyst, which affects the absolute values obtained very considerably.

The determination of the partial vapour pressure of hydrogen chloride in alcohol in presence and in absence of water vapour served to connect the behaviour of water in the reactions previously discussed with its influence on the more directly measurable properties of solution. It was shown that the partial pressures of the hydrogen chloride are reduced very

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[1] *J. Chem. Soc.*, 1911, **99**, 917 *et seq.*

considerably by the presence of small quantities of water, as is evident from the graphical representation in Fig. 20, the relative depression increasing, moreover, as the concentration of acid diminishes.

The reduction caused by water on the electromotive force of the hydrogen electrode in alcoholic hydrogen chloride, investigated in the same laboratories,[1] has also been used as evidence of the point of view here set forth in explanation of the anti-catalytic effect of water in esterification processes.

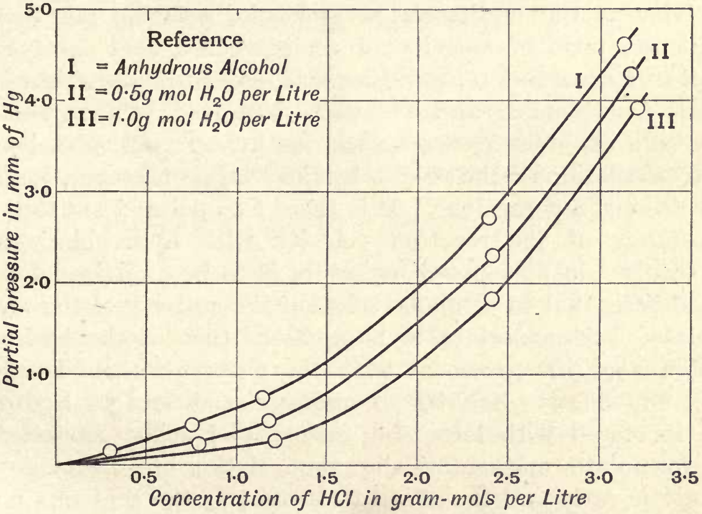

FIG. 20.

The influence of additions of neutral salts possessing an anion in common with that of the catalysing acid was next investigated by Goldschmidt and led to further remarkable conclusions. It was shown, for example, that addition of chlorides was without influence on the velocity of esterification, using hydrochloric acid as catalyst.[2] With weaker acids, addition of neutral salts repressed the velocity of esterification. The retardation was, however, by no means proportional to the hydrogen-ion concentration, as calculated by application of the mass action law to the electrolytic dissociation of the

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[1] See Hardman and Lapworth, *J. Chem. Soc.*, 1912, **101**, 2249.

[2] Goldschmidt, *Zeitsch. Elektrochem.*, 1909, **15**, 4.

acid in presence of a salt having a common ion. Instead, it was shown that addition of excess of salt repressed the velocity of reaction to a definite lower limit and no further. Goldschmidt associated these observations with the conclusion that the undissociated molecules of catalyst are also active, and calculated out his experimental results in accordance with this view.[1] The relation between the catalytic activity of the undissociated molecule and the strength of the acid was pointed out by Snethlage,[2] who showed from Goldschmidt's figures that the stronger the acid the greater the catalytic activity of the undissociated molecule, pointing out further that the ratio of activity of undissociated acid catalyst to that of hydrogen ion should be independent of the acid esterified. Goldschmidt and Thuessen demurred to this view as a result of investigations with methyl alcohol as solvent.[3] A recalculation of the results by Snethlage,[4] however, justifies the original assumptions. It is there also pointed out that the constancy of the reaction velocity with hydrochloric acid as catalyst in presence of chlorides is to be explained by the hypothesis that in alcoholic solution the activity of the undissociated hydrochloric acid is equal to that of the hydrogen ion, a view in agreement with the observation made above that the relative activity of undissociated acid to hydrogen ion increased with increasing strength of acid. An attempt to formulate mathematically the relationship between the catalytic ratio and the affinity constant of the acid was made by Taylor,[5] but without theoretical development.

The complexity of the esterification process is manifest from these researches. It is evident that the operation of a number of equilibria are determining factors in the velocity with which esterification occurs. These include the actual electrolytic dissociations of the catalyst and esterified acid, the equilibria between the ions, the undissociated molecules, and the alcohol solvent, as well as the disturbing equilibria brought about by the intervention in the reaction of the water produced in the esterification process. In addition, also, the possibility of ter-molecular complexes in the case

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[1] *Zeitsch. Elektrochem.*, 1911, **17**, 684.

[2] *Ibid.*, 1912, **18**, 539.

[3] *Zeitsch. physikal. Chem.*, 1913, **81**, 30.

[4] *Ibid.*, 1913, **85**, 238.

[5] *Zeitsch. Elektrochem.*, 1914, **20**, 201.

of the non-autocatalytic reactions cannot be excluded. The direct or autocatalytic esterification process has been regarded by most workers as differing in detail from the catalytic process, and it may be in the possibilities and stability of complex formations as much as in the factors of acid strength, that the differences lie. A deeper study of this subject from such a point of view would doubtless show that the differences observed are reconcilable to the general underlying principles which have been put forward.

HETEROGENEOUS ESTERIFICATION

Esterification in the gaseous phase in presence of oxides as catalysts has been studied by Sabatier and Mailhe.[1] When an alcohol and an acid are simply passed through a heated tube little or no reaction occurs in the sense of the equation :

$$R{\cdot}COOH + R_1{\cdot}OH = R{\cdot}COOR_1 + H_2O \quad . \quad . \quad (1)$$

If a charge of certain oxides, as for example, TiO_2, be placed in the tube, rapid reaction with production of high concentrations of ester will result at a temperature of 280–300°.

It has been shown in a preceding section (p. 288) that oxides are effective catalytic agents in promoting the dehydration of alcohols with hydrocarbon formation, according to the equation :

$$C_nH_m{\cdot}OH \rightarrow C_nH_{m-1} + H_2O \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It will later be shown that the same agents are also active in promoting the decomposition of acids with elimination of water and carbon dioxide to form ketones, as generalised by the equation :

$$2R{\cdot}COOH \rightarrow CO_2 + H_2O + R{\cdot}COR \quad . \quad . \quad . \quad (3)$$

It will, therefore, be obvious that in order to promote etherification according to equation (1), due regard must be paid in the choice of catalyst to the possibility of occurrence of the reactions (2) and (3).

Thus it might be anticipated that thoria, which is a very efficient agent in the dehydration of alcohols and also in the

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[1] *Compt. rend.*, 1910, **150**, 823.

decomposition of fatty acids to ketones, would not be the most suitable agent for promoting esterification in the gaseous phase. On the contrary, with aromatic acids where the tendency for reaction (3) to occur is much less, thoria may be used very effectively as an esterification agent—and was so utilised by Sabatier and Mailhe in the synthesis of numerous esters of benzoic and toluic acids, *e.g.* :

$$C_6H_5{\cdot}COOH + C_2H_5{\cdot}OH \rightarrow C_6H_5{\cdot}COO{\cdot}C_2H_5 + HOH.$$

The ease with which this reaction proceeds points to the fact, which is confirmed by the subsequent examples, that dehydration from an acid and an alcohol jointly occurs much more readily than dehydration of an alcohol alone.

For the synthesis of fatty acid esters, the choice of titania as catalyst was justified by the results. It will be observed from its position in the table cited in the section on dehydration (p. 288) that titania is much less active as a dehydrating agent than thoria, and this is likewise true for its action on fatty acids. At 280–300°, however, its dehydrating action on alcohol and fatty acid jointly is very effective, and thus can be used for the synthesis of the most varied fatty acid esters.

The influence of temperature on the position of equilibrium prevailing in an acid–alcohol ester–water system was investigated by Berthelot in a study of the autocatalytic esterification of ethyl alcohol and acetic acid.

Reaction temperature.	Equilibrium percentage of ester.
Room.	65·2
100°	65·6
170	66·5
200	67·3

The figures obtained show an increase of the equilibrium concentration of ester with increase of temperature. This is relatively small, however, as might be anticipated from the thermal data for the reaction, which show a very small temperature effect for the heat of reaction and therefore a correspondingly small change in the equilibrium as calculated from the van't Hoff equation :

$$\frac{d \log K}{dt} = - \frac{Q}{RT^2}.$$

Sabatier and Mailhe confirm the results of Berthelot by indicating from the results obtained by them at the reaction temperatures employed for their catalytic process a somewhat higher equilibrium concentration of ester than that given by Berthelot at the highest temperature employed by him in his experiments.

The preference of esterification over dehydration in presence of suitable oxide catalysis is also indicated by the fact that good yields of ester can be obtained even with secondary alcohols. Thus, at a temperature of 300° isopropyl alcohol may be esterified without the simultaneous production of propylene, whereas, with the alcohol alone rapid dehydration sets in with production of the hydrocarbon at a temperature of 260°.

SYNTHESIS OF AMINES

The suppression of the simple dehydration process which alcohols undergo in presence of catalysts is also beautifully illustrated, when gaseous ammonia is admixed with the alcohol vapour in its passage over an oxide catalyst. Dehydration occurs, the elements of water being removed, however, from alcohol and ammonia jointly, with simultaneous production of an amine according to the equation :

$$C_nH_{2n+1}\cdot OH + NH_3 \rightarrow H_2O + C_nH_{2n+1}\cdot NH_2.$$

Investigations of Sabatier and Mailhe[1] have shown that this process is generally applicable in the synthesis of amines. It is produced readily in presence of thoria at temperatures of 300–350° without production of ethylenic hydrocarbon. With the other oxides cited in the earlier table as possessing mixed dehydrating and dehydrogenation properties, the production of amines is equally possible without accompaniment of ethylenic hydrocarbon or hydrogen as side products. The formation of amine completely predominates.

By substitution of a primary amine for ammonia in the entering vapours, the product obtained is a secondary amine :

$$R\cdot OH + R_1\cdot NH_2 = R_1N\cdot HR + H_2O.$$

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[1] *Compt. rend.*, 1910, **150**, 823.

This forms a general method for the preparation not only of symmetrical secondary amines—which result in small quantity as a secondary reaction in the dehydration of ammonia and alcohol—but also of mixed secondary amines.[1] Thus from ethyl alcohol and isoamylamine, secondary ethyl isoamylamine is readily obtained. Similarly, also, alkyl derivatives of piperidine may be obtained.[2]

SYNTHESIS OF THIOLS

By a procedure analogous to that just detailed for the synthesis of amines, it is possible to effect the synthesis of thiols. The dehydration of alcohols admixed with sulphuretted hydrogen by means of oxide catalysts at temperatures in the interval of 300–380° forms a general method of preparation of thiols from the corresponding alcohol :

$$C_nH_m{\cdot}OH + H_2S \rightarrow C_nH_m{\cdot}SH + H_2O.$$

The reaction may be accompanied by further dehydration of thiol and alcohol to produce the corresponding sulphide according to the equation :

$$C_nH_m{\cdot}SH + C_nH_m{\cdot}OH = (C_nH_m)_2S + H_2O.$$

Of the oxide catalysts employed, thoria has proved the best, the yields of thiol with the simpler primary aliphatic alcohols exceeding 75 per cent. The side reaction producing ethylenic hydrocarbon is small in such cases, but with secondary alcohols it is considerable, and the yields seldom exceed 30 per cent.

The yield of thiol per 100 parts of isoamyl alcohol decomposed decreases with the oxide catalyst employed to the extent shown in the following table :

ThO_2	70	W_2O_3	22
ZrO_2	44	Cr_2O_3	18
UO_2	30	Mo_2O_5	17
		Al_2O_3	10

With the catalytic agents of small efficiency the product is mainly amylene.

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[1] Sabatier and Mailhe, *Compt. rend.*, 1909, **148**, 900.

[2] Gaudion, *Bull. Soc. chim.*, 1911, (iv), **9**, 417.

Phenols at a somewhat higher temperature range of 430–480° yield the corresponding aromatic thiols :

$$C_6H_5{\cdot}OH + H_2S = C_6H_5{\cdot}SH + H_2O,$$

but only in small quantities, the yields never exceeding 10 per cent.[1]

DEHYDRATION OF ALDEHYDES AND KETONES

Condensation of several molecules of aldehydes or ketones, with simultaneous elimination of water, is promoted by various dehydrating agents common in organic technique such as sodium or potassium hydroxide, sodium acetate, dry hydrogen chloride, zinc or aluminium chlorides.

In the case of aldehydes, the product is in general a higher unsaturated aldehyde, as, for example, in the case of acetaldehyde, which is slowly transformed by boiling with aqueous sodium acetate or zinc chloride into crotonic aldehyde, according to the reaction (see also p. 323) :

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO \rightarrow CH_3{\cdot}CH{:}CH{\cdot}CHO + H_2O.$$

The analogous reaction with acetone is provided by reagents such as aluminium chloride, sodium or lime, yielding, even at the ordinary temperature with long contact, mesityl oxide in the first place and then phorone :

$$\begin{gathered}2CH_3{\cdot}CO{\cdot}CH_3 \rightarrow (CH_3)_2{:}C{:}CH{\cdot}CO{\cdot}CH_3 + H_2O \rightarrow \\ (CH_3)_2{:}C{:}CH{\cdot}CO{\cdot}CH{:}C(CH_3)_2\end{gathered}$$

Condensation with elimination of water between mixed aldehydes and ketones is similarly possible, especially with aromatic aldehydes. Thus :

$$(1)\quad C_6H_5{\cdot}CHO + CH_3{\cdot}CO{\cdot}CH_3 \rightarrow C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3 + H_2O$$

$$(2)\quad 2C_6H_5{\cdot}CHO + CH_3{\cdot}CO{\cdot}CH_3 \rightarrow (C_6H_5{\cdot}CH{:}CH)_2CO + 2H_2O.$$

The variations of this reaction are manifold, and the agencies employed have likewise been multiplied in organic synthesis—generalisation or systematisation of the change are impossible.

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[1] Sabatier and Mailhe, *Compt. rend.*, 1910, **150**, 1220.

since they have been little studied from the theoretical point of view—doubtless due in a degree to the slowness of the reaction velocity.

DEHYDRATION OF ALDEHYDE-ALCOHOL MIXTURES

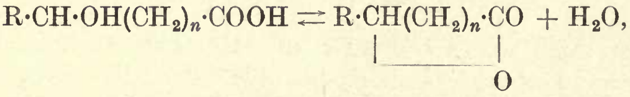
Dry hydrogen chloride is the normal catalytic agent[1] for simultaneous dehydration of mixtures of alcohol and aldehyde, the product of reaction being the acetals. The aldehyde is added to a 1 per cent. solution of hydrogen chloride in the alcohol and reaction is allowed to take place in the cold:

$$R\cdot CH\cdot O + 2R'\cdot OH \rightarrow R\cdot CH(OR')_2 + H_2O.$$

If heat be employed to accelerate the reaction, the yields diminish owing to the hydrolytic influence on the product of the catalyst employed. The same catalytic agent promotes the action of aldehydes and alcohols to form acetals with the simultaneous employment of ethyl orthoformate.

SYNTHESIS OF LACTONES

The elimination of water from hydroxy-acids with formation of lactones is a dehydration process catalytically accelerated by acids. The reaction occurring, which may be generalised as follows:



$$R\cdot CH\cdot OH(CH_2)_n\cdot COOH \rightleftharpoons \underbrace{R\cdot CH(CH_2)_n\cdot CO}_{O} + H_2O,$$

is the result of an equilibrium between two opposed reactions, which, in presence of acids in dilute aqueous solution, where the concentration of water may be regarded as constant, are monomolecular and are both catalytically promoted by addition of acids. The reaction velocity in such a process is given by the equation:

$$\frac{dx}{dt} = k_1(a - x) - k_2x,$$

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[1] E. Fischer and Groebe, *Ber.*, 1897, **30**, 3053.

where a is the initial concentration of hydroxy-acid, x the amount transformed at time t, k_1 and k_2 the reaction constants of lactone formation and the reverse hydrolysis respectively in presence of the added acid.

If the equilibrium constant of the reaction be K, then

$$K = \frac{k_1}{k_2}$$

and consequently

$$\frac{dx}{dt} = k_2K(a - x) - k_2x,$$

and this expression on integration yields, as was shown by P. Henry,[1] the equation :

$$k_1 + k_2 = \frac{1}{t} \log \frac{Ka}{Ka - (K + 1)x}.$$

The equation gives values for the sum of the two reactions in terms of the equilibrium constant and the quantities of acid and lactone present at the times t_0 and t. It was tested experimentally by Henry in the case of hydroxybutyric acid, good reaction constants for $(k_1 + k_2)$ being found with the aid of the experimentally determined equilibrium constant $K = 2{\cdot}68$. In the conversion of oxyvaleric acid to valerolactone, it was found that the equilibrium concentration of lactone is more than 92 per cent. of the original concentration of hydroxy-acid, so that the influence of the reverse reaction on the velocity of lactone formation was small, and the process occurring could be treated as a simple monomolecular reaction with the velocity equation :

$$k_1 = \frac{1}{t} \log \frac{a}{a - x},$$

to which obviously also the above equation for the two opposing reactions reduces when $K = \frac{k_1}{k_2}$ becomes large in comparison with the other magnitudes.

Studied thus as a monomolecular reaction, it was shown by Henry that the conversion of oxyvaleric acid to valero-

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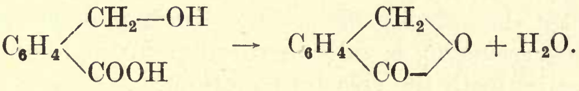
[1] *Zeitsch. physikal. Chem.*, 1892, **10**, 98.

lactone was catalytically accelerated by acids in proportion to the concentration of the hydrogen ions. A more exact study of this reaction[1] in presence of varying concentrations of catalysing acid with and without the addition of neutral salts having a common ion, has shown that the proportionality to hydrogen-ion concentration is not, however, an exact one, but that the deviations are analogous in every way to those already observed and noted in the case of catalytic hydrolysis and synthesis of esters, and that therefore the same explanations of mechanism of the catalytic activity may also be employed in this case.

Since hydrogen ions are catalytically active in promoting lactone formation, it is obvious that the hydrogen ions formed by solution of the acid itself in water will accelerate the reaction—another example of autocatalysis. Furthermore, since in the progress of autocatalytic action the concentration of hydroxy-acid is progressively diminished with formation of lactone, it is obvious, also, that the auto-catalytic activity, and consequently the rate of reaction, will diminish. The reaction thus affords an interesting example of auto-retardation. The influence of these two factors of auto-catalysis and auto-retardation on the velocity of lactone formation in aqueous solution was specially investigated and mathematically formulated by Collan[2] in a study of the conversion of carboxybenzyl alcohol to the cyclic lactone, phthalide :



$$C_6H_4\left\langle\begin{matrix}CH_2{-}OH\\ COOH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CH_2\\ CO{-}\end{matrix}\right\rangle O + H_2O.$$

DEHYDRATION OF FATTY ACIDS

Attempts to eliminate water from the aliphatic acids are, with the exception of formic acid, only achieved with simultaneous evolution of carbon dioxide and rupture of the molecule, the product being ketonic or aldehydic in nature.

Formic acid may be decomposed in several ways and in

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[1] Taylor and Close, *J. Amer. Chem. Soc.*, 1917, **39**, 422.

[2] *Zeitsch. physikal. Chem.*, 1892, **10**, 100.

presence of certain catalysts with elimination of water. Thus, the possibilities may be formulated by the equations :

$$\begin{aligned}&(1)\ \mathrm{H{\cdot}COOH} \rightarrow \mathrm{H_2O + CO},\\&(2)\ \mathrm{2H{\cdot}COOH} \rightarrow \mathrm{H{\cdot}CHO + CO_2 + H_2O},\\&(3)\ \mathrm{3H{\cdot}COOH} \rightarrow \mathrm{CH_3{\cdot}OH + CO_2 + H_2O},\end{aligned}$$

whilst dehydrogenation may simultaneously occur in effecting one or other dehydration process according to the reaction :

$$\mathrm{H{\cdot}COOH} \rightarrow \mathrm{CO_2 + H_2}.$$

The primary process of dehydration to yield carbon monoxide and water is that normally occurring on treatment of formic acid with strong dehydrating agents such as sulphuric acid or anhydrous oxalic acid. The reversibility of this process has long been known, and is the basis of modern technical practice for the synthesis of formic acid. Actually, use is made of a base such as soda, the product being, therefore, a formate. The equilibrium occurring in the process is calculable according to the Nernst heat theorem from the thermal constants of the reacting substances.

Thus for the gas reaction, according to Pollitzer,[1] the heat of reaction,

$$\mathrm{CO + H_2O = H{\cdot}COOH} + 9300 \text{ cal.},$$

can be obtained from the heats of combustion, and amounts to 9,300 cal. for gaseous formic acid. Utilising the Nernst approximation formula and values for the "chemical constant,"

$$C_{\mathrm{H_2O}} = 3{\cdot}6,\ C_{\mathrm{CO}} = 3{\cdot}5,\ C_{\mathrm{H\cdot COOH}} = 3{\cdot}5,$$

there follows for the equilibrium equation :

$$\log \frac{p_{\mathrm{CO}}p_{\mathrm{H_2O}}}{p_{\mathrm{H\cdot COOH}}} = -\frac{9300}{4{\cdot}571T} + 1{\cdot}75 \log T + 3{\cdot}8,$$

which gives the following values for K :

$T^\circ =$	300°	500°	1000° abs.
$K =$	20	3×10^4	10^7.

According to this result, formic acid decomposes practically

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[1] *Berechnung chemischer Aff. Ahrens Sammlung*, 1912, p. 443.

quantitatively to carbon monoxide and water when but slightly heated. On the other hand, the equilibrium concentration of the acid at the ordinary temperature should be demonstrable, especially if increased by application of pressure to the system.

In the researches of Branch[1] the equilibria prevailing at 156° and 218° with gas–liquid phases were actually determined. It was shown that the decomposition was reversible and that mineral acids, especially hydrochloric acid, acted as catalysts.

The equilibrium constants given by the measurements represent that of the reaction :

$$H\cdot COOH_{1M} = H_2O_{liq} + CO$$

the values of K being 89·9 and 310 at 156° and 218°, when the CO concentration was expressed in atmospheres pressure, that of the formic acid in mols. per litre, the water as the ratio of its concentration to that in pure water.

It was shown that with $\frac{1}{2}N$-hydrochloric acid as catalyst no appreciable side reactions occurred, the gas formed being pure carbon monoxide.

Sabatier and Mailhe[2] have shown that in the vapour phase various oxide catalysts act similarly. Thus oxide of titanium at 170–320° gives carbon monoxide in a marked degree of purity, and this is true also of blue oxide of tungsten at 270°. Alumina, silica, zirconia, and uranous oxide give mainly carbon monoxide, but a certain proportion of formaldehyde is simultaneously formed according to reaction (2). With uranous oxide, this latter reaction is almost as important as the simple dehydration process. With thoria, the change commences at 250–375°, with production of all the products of dehydration. The proportions of each progressively alter with rise in temperature of decomposition. At 250°, the gaseous product contains 73 per cent. CO, 15 per cent. CO_2 and 10 per cent. H_2, together with a small quantity of liquid formaldehyde. At 320°, there is about 45 per cent. CO in the gas and considerable quantities of the condensation product of formaldehyde and methyl alcohol. This latter increases in percentage with increase in temperature, due to the further decomposition of formaldehyde to carbon monoxide and hydrogen.

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[1] *J. Amer. Chem. Soc.*, 1915, **37**, 2316.

[2] *Compt. rend.*, 1911, **152**, 1212.

SYNTHESIS OF KETONES

With the aid of oxide catalysts, the fatty acids higher than formic acid yield, on heating, symmetrical ketones with simultaneous elimination of water and carbon dioxide :

$$2\mathrm{R{\cdot}COOH} \rightarrow \mathrm{R{\cdot}CO{\cdot}R} + \mathrm{CO_2} + \mathrm{H_2O}.$$

As is well known, dry distillation of the calcium or barium salts of the fatty acids yields the corresponding ketone. The transformation of this process to a catalytic reaction was suggested by Squibb,[1] who proposed to pass the vapour of acetic acid over barium carbonate heated to 500°. As early as 1902, this process, according to Conroy,[2] was said to be applied industrially, yields of more than 90 per cent. being possible. In the later of the two papers cited, Squibb records the decomposition to 90 per cent. acetone of 1,700 lb. of absolute acetic acid in a large rotatory still 12 feet long by 2 feet diameter during a period of 126 hours. This would correspond with a conversion of approximately one-third of a pound of acetic acid per cubic foot of catalyst space per hour. Precipitated carbonate constitutes an efficient catalyst, action being rapid at 450°. The activity of the catalyst is of long duration, in spite of slight carbonisation, and naturally at such temperatures in presence of such a partial pressure of carbon dioxide exists entirely in the form of carbonate.

Ipatiev and Schulmann[3] and Mailhe[4] extended the list of catalysts to zinc oxide and carbonate, cadmium oxide, and chromium oxide, whilst Senderens[5] showed that alumina and thoria operated efficiently in the neighbourhood of 350–400°. The yields are high, and the activity is constant; in the case of thoria, revivification of the catalyst can be effectually carried out by simple ignition.

Ferrous oxide is a suitable catalytic agent for the production of ketones from the higher fatty acids. Thus, with stearic acid, an 80 per cent. yield of stearone may be obtained.

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[1] *J. Amer. Chem. Soc.*, 1895, **17**, 187 ; 1896, **18**, 231.

[2] *J. Soc. Chem. Ind.*, 1902, **21**, 309.

[3] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 764.

[4] *Memoire Ac. des Sc. Toulouse*, 1907.

[5] *Bull. Soc. chim.*, 1908, (iv), **3**, 824.

Modern plants for the manufacture of synthetic acetone employ such catalytic agents, with economies in the operating temperatures and in the yield of product. Thus it is possible, by means of a three-stage process, each stage catalytic in nature, to proceed from alcohol to acetone. The conversion of alcohol to aldehyde is a typical dehydrogenation process, as earlier outlined. Oxidation of aldehyde yields acetic acid, and dehydration of this with elimination of carbon dioxide results in acetone. The possibilities elsewhere outlined for production of alcohol on the technical scale by catalytic processes, taken in conjunction with the present application, illustrate in a marked manner the penetration of the catalytic reaction into modern industry.

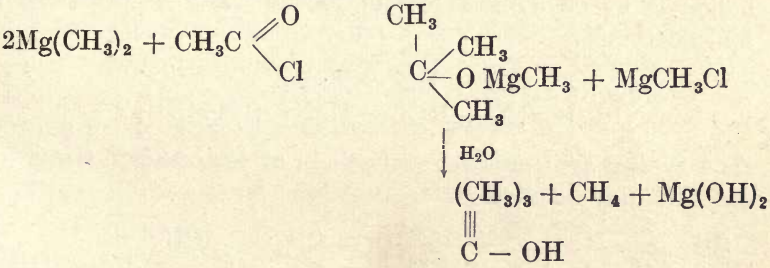
CHAPTER X

APPLICATIONS OF CATALYSIS TO ORGANIC CHEMISTRY

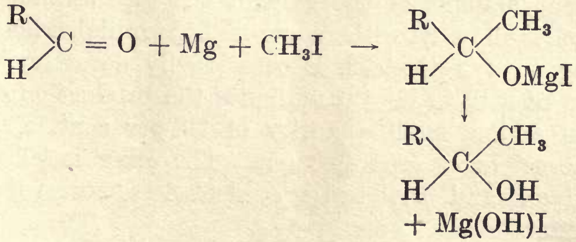
THE GRIGNARD REAGENT

THE use of organo-metallic compounds in organic synthesis may be said to date from the time of Frankland[1] and Cahours,[2] but it was not until Löhr isolated magnesium diethyl in 1890 that the development of synthetic operations by means of these reagents became generally possible.

In 1893, Fleck performed the first synthesis with the new reagent, converting an acetyl chloride into a tertiary alcohol :



Barbier, in 1899, showed that it was unnecessary to isolate the magnesium alkyls for synthesis. Thus an aldehyde could be converted into a secondary alcohol by interaction with magnesium powder and an alkyl halide :



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[1] *Annalen*, 1849, **71**, 203.

[2] *Compt.. rend.*, 1859, **49**, 1110.

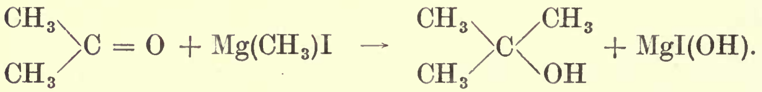
Grignard, Barbier's pupil, made the interesting discovery, a year later, that ether acted as a catalytic agent in the process, and that when this agent was present the reactions proceeded smoothly and good yields were obtained.[1]

All the metals of the uneven series of the Mendeléeff table yield organo-metallic compounds, with the exception of copper and silver, whilst calcium, potassium, and lithium of the even series also form similar compounds. Nevertheless, with the exception of the calcium alkyls, suggested by Beckmann[2] in 1905, magnesium is practically exclusively employed.

The preparation of the reagent is a simple matter. Equivalents of magnesium turnings and the alkyl halide with half its volume of ether are allowed to react under a spiral reflux condenser. If the flask and its contents are dry, the reaction commences immediately; if not, it is usually found efficacious to add a small quantity of some previously prepared reagent or a trace of iodine as suggested by Baeyer. Excess of alkyl halide is to be avoided owing to the possible formation of hydrocarbons:

$$\mathrm{Mg} + \mathrm{RX} \rightarrow \mathrm{MgRX}$$
$$\mathrm{MgRX} + \mathrm{R_1X} \rightarrow \mathrm{MgX_2} + \mathrm{R{\cdot}R_1}.$$

As a typical synthesis the conversion of acetone into trimethyl carbinol may be cited:



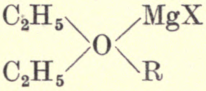
$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\mathrm{C}=\mathrm{O} + \mathrm{Mg(CH_3)I} \rightarrow \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\mathrm{C}<\!\!\begin{matrix}\mathrm{CH_3}\\ \mathrm{OH}\end{matrix} + \mathrm{MgI(OH)}.$$

A cool solution of acetone in ether (containing half its volume of ether) is allowed to drop on to 5 per cent. more than the equivalent amount of the reagent. A greenish mass settles out which is allowed to stand over-night; for higher homologues, warming on a water-bath is occasionally necessary. On the addition of a little ice (to minimise the production of hydrocarbons) and a small quantity of 30 per cent. acetic acid, the ethereal layer separates out. The ether is subsequently distilled off and the tertiary alcohol removed by steam distillation.

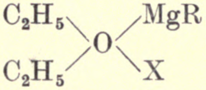
[1] *Compt. rend.*, 1900, **130**, 1322.

[2] *Ber.*, 1905, **38**, 904.

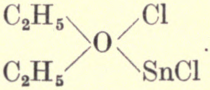
The mechanism of the Grignard reaction has not been definitely settled. Grignard himself showed that an additive compound was formed with the ether, $MgRX(C_2H_5)_2O$, and suggested the structural formula :



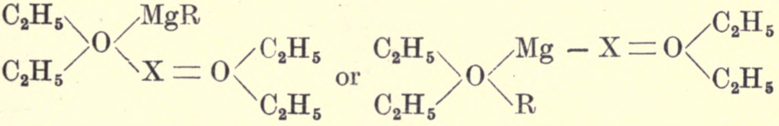
in the form of an oxonium compound. Baeyer and Villiger suggested as alternative :



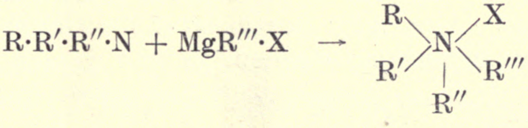
comparable with :



Tschelinzeff[1] in 1905 isolated MgRX by performing the operation in benzene solution, using a trace of ether as catalytic agent and studied the heat of formation of the ether magnesium alkyl halide complex. He obtained the rather surprising result that apparently 2 molecules of ether took part in the reaction ($C_3H_7MgI + Et_2O = 6{\cdot}63$ kg. cal. $C_3H_7Mg{\cdot}IEt_2O + Et_2O = 5{\cdot}66$ kg. cal.), indicating the existence of a secondary oxonium linkage :



Tertiary amines also catalyse the reaction and presumably form complexes :



It is evident that isomers may be expected on either Baeyer's or Grignard's formula ; the Grignard structural formula,

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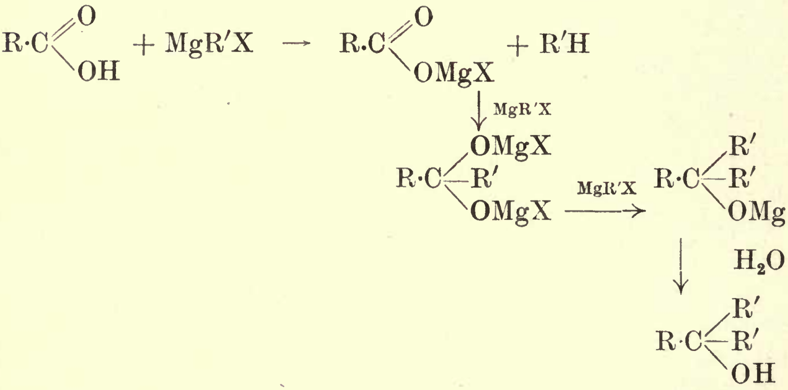
[1] *Ber.*, 1905, **38**, 3664.

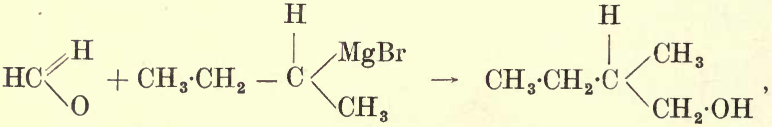
however, is usually adopted, since it indicates more easily the various reactions which may be performed with the reagent.

A great variety of syntheses may be accomplished with the aid of the Grignard reagent; we have already noted the preparation of secondary and tertiary alcohols from aldehydes and ketones, and the formation of hydrocarbons from alkyl halides and magnesium methyl. Amongst other equally important synthetic operations, the following may be briefly cited.

(*a*) The conversion of acids and esters to alcohols:



(*b*) Formaldehyde will naturally give a primary alcohol,[1] thus:



the product being racemic amyl alcohol.

(*c*) Phenols, thiophenols, selenophenols, and their homologues[2] can be formed by treatment of the Grignard reagent with oxygen, sulphur or selenium. Thus:

$$C_6H_5{\cdot}MgBr + S \rightarrow C_6H_5{\cdot}SH.$$

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[1] See Tissier and Grignard, *Compt. rend.*, 1902, **134**, 107; Zelinsky, *Ber.*, 1908, **41**, 2628; Freundler and Damond, *Compt. rend.*, 1906, **141**, 830.

[2] Bouveault, *Bull. Soc. chim.*, 1903, **29**, 1051; Wuyts and Cosyns, *ibid.*, 1903, **29**, 689.

Small quantities of the compound $C_6H_5{\cdot}S{\cdot}S{\cdot}C_6H_5$ are usually formed at the same time.

(*d*) Treatment with carbon dioxide in a similar manner will yield carboxyl derivatives, thus:

$$C_6H_5MgBr + CO_2 \rightarrow C_6H_5{\cdot}COOH$$
$$2C_6H_5MgBr + CO_2 \rightarrow (C_6H_5)_2{\cdot}CO$$
$$3C_6H_5MgBr + CO_2 \rightarrow (C_6H_5)_3{\cdot}COH$$

Carbon oxysulphide and carbon disulphide, in a similar manner, give thiocarbonic acids, whilst sulphur dioxide yields sulphinic acids. Thus:

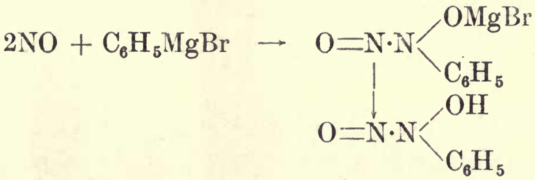
$$SO_2 + C_6H_5MgBr \rightarrow C_6H_5{\cdot}SO_2MgBr \rightarrow C_6H_5{\cdot}SO_2H.$$

(*e*) The preparation of esters can easily be accomplished by the use of chloroformic ester as illustrated by the equation:

$$Cl{\cdot}COO{\cdot}C_2H_5 + C_6H_5MgBr. \rightarrow C_6H_5{\cdot}COO{\cdot}C_2H_5 + MgBr.Cl.$$

Application of the Grignard reagent to synthesis in the carbohydrate group have been made by Paal,[1] Frankland and Twiss,[2] to the terpenes by Perkin,[3] Hesse,[4] Mills and Bain,[5] and others. Kipping[6] has made use of the reagent in the synthesis of organo-silicon compounds. Pope and Peachey effected the resolution of certain tin compounds thus prepared, whilst Pfeiffer[7] attempted the preparation of lead and mercury alkyl derivatives with its aid.

Not less important are the reactions of the Grignard reagent with organic nitrogen compounds. In 1902, Sand and Singer prepared nitrosophenyl hydroxylamine by the following reaction:



$$2NO + C_6H_5MgBr \rightarrow O{=}N{\cdot}N\begin{cases}OMgBr\\C_6H_5\end{cases} \downarrow\ O{=}N{\cdot}N\begin{cases}OH\\C_6H_5\end{cases}$$

Wieland's attempts to prepare $R{\cdot}NOO{\cdot}H$ from nitrogen peroxide yielded only substituted hydroxylamines, possibly owing to reaction of the NO_2 as the polymer N_2O_4.

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[1] See *Ber.*, 1905, **38**, 1686; 1906, **39**, 1301, 2823, 2827.

[2] *J. Chem. Soc.*, 1905, **87**, 864.

[3] *Ibid.*, 1907, **91**, 480.

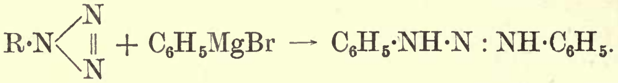
[4] *Ber.*, 1909, **42**, 1127.

[5] *J. Chem. Soc.*, 1910, **97**, 1866.

[6] *Ibid.*, 1901 to 1909.

[7] *Ber.*, 1904.

Dennis and Brown[1] and Dimroth[2] prepared triazine derivatives from alkyl azides,

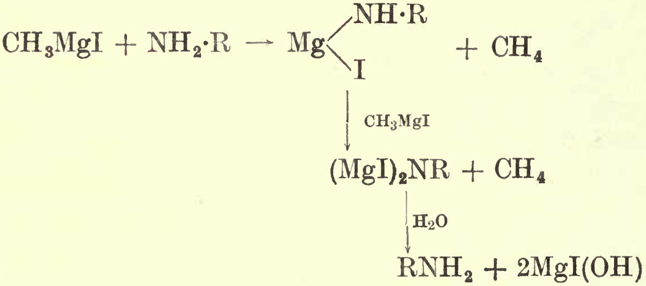


$$R{\cdot}N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + C_6H_5MgBr \rightarrow C_6H_5{\cdot}NH{\cdot}N:NH{\cdot}C_6H_5.$$

Amides can be converted into ketones. Thus:

$$\begin{aligned}R{\cdot}CO{\cdot}NH_2 + 2R'MgX \rightarrow\ & RC{\cdot}R'{\cdot}OMgX{\cdot}NHMgX.\\ & \downarrow\\ & R{\cdot}R'{\cdot}COH{\cdot}NH_2 + MgX_2 + Mg(OH)_2\\ & \downarrow\\ & R{\cdot}R'{\cdot}CO + NH_3,\end{aligned}$$

whilst the amines yield hydrocarbons[3] from the Grignard reagent



$$\begin{aligned}CH_3MgI + NH_2{\cdot}R \rightarrow\ & Mg\left\langle\begin{matrix}NH{\cdot}R\\ I\end{matrix}\right. + CH_4\\ & \Big\downarrow{\scriptstyle CH_3MgI}\\ & (MgI)_2NR + CH_4\\ & \Big\downarrow{\scriptstyle H_2O}\\ & RNH_2 + 2MgI(OH)\end{aligned}$$

These examples serve to indicate the great importance of the Grignard reagent as a synthetic agent in organic chemistry, not only on account of its varied activity, but also by reason of the ease with which most of the reactions may be carried out.

THE FRIEDEL-CRAFTS' REACTION

In 1877, Friedel and Crafts[4] showed that anhydrous aluminium chloride was an extraordinarily effective catalytic agent for bringing about condensations of the type:

$$C_6H_6 + RX + (AlCl_3) \rightarrow C_6H_5 - R + HX,$$

where RX is an alkyl halide.

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[1] *J. Amer. Chem. Soc.*, 1901, **26**, 104, 577. [2] *Ber.*, 1905, **38**, 670, 1573.

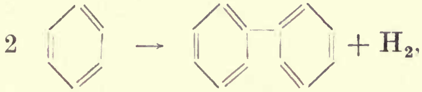
[3] Sudborough and Hibbert, *J. Chem. Soc.*, 1904, **85**, 933.

[4] *Compt. rend.*, 1877, **84**, 1392.

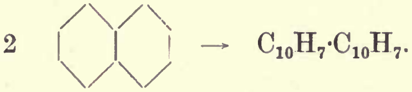
The researches of Jacobsen[1] and of Anschütz[2] have shown that the reaction is reversible. Thus if hydrochloric acid gas be passed into a mixture of toluene and aluminium chloride benzene may be obtained.

Substitution usually proceeds further than the stage indicated above. Thus, from benzene and methyl chloride in excess, methylation of the benzene ring can proceed to completion. Even when the proportions necessary for the preparation of toluene are taken, the yield is far from theoretical and the product has to be freed by fractionation from the xylenes and mesitylene present.

At higher temperatures the aromatic hydrocarbons, benzene or naphthalene will react, undergoing a process of dehydrogenation (see p. 219). Thus :



and as shown by Miss Homer, these changes take place much more readily with naphthalene



A similar reaction takes place with the acid chlorides in presence of aluminium chloride forming ketones.

$$R \cdot CO \cdot Cl + (AlCl_3) + C_6H_6 \rightarrow R \cdot CO \cdot C_6H_5 + (AlCl_3) + HCl.$$

Utilising carbonyl chloride and subsequently submitting the acid chloride thus formed to hydrolysis, acids may similarly be prepared.

$$COCl_2 + AlCl_3 + C_6H_6 \rightarrow C_6H_5 \cdot COCl \rightarrow C_6H_5 \cdot COOH.$$

The method was extended by Gattermann[3] to the preparation of aldehydes by passing a mixture of dry hydrogen chloride and carbon monoxide into benzene in the presence of aluminium chloride or cuprous chloride :

$$C_6H_6 + CO + HCl + (AlCl_3) \rightarrow C_6H_5 \cdot CHO + HCl + (AlCl_3)$$

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[1] *Ber.*, 1885, **18**, 339.

[2] *Ibid.*, 1885, **18**, 657.

[3] *Annalen*, 1906, **347**, 347.

Anhydrous ferric chloride, cuprous chloride or the finely divided metals such as zinc, copper, aluminium or amalgamated aluminium have all been suggested as alternative catalytic agents, but, with the exception of cuprous chloride used in Gattermann's reaction, they are all less active than anhydrous aluminium chloride.

The mechanism of the reaction.—In 1901, Perrier isolated from the interaction of aluminium chloride and an acyl chloride in solutions of carbon disulphide crystalline compounds of the formula $R{\cdot}CO{\cdot}Cl{\cdot}AlCl_3$, whilst a year later Koller showed by cryoscopic measurements that these molecular compounds were complex, having a molecular composition $(R{\cdot}CO{\cdot}ClAlCl_3)_2$.

Steele[1] systematically investigated the kinetics of the reaction.

A stream of dry hydrogen was passed through a toluene wash-bottle into a reaction mixture of benzyl chloride and the catalyst (aluminium chloride or ferric chloride), the rate of evolution of hydrochloric acid in the gas stream being measured.

The ratio of catalyst to benzyl chloride was varied within wide limits. It was noted in the preparation of hydrocarbons that there was a small period of induction, the solution becoming of an intense orange colour suggesting the formation of a complex $(C_6H_5{\cdot}CH_2Cl{\cdot}AlCl_3)_2$.

With ferric chloride, the period of induction was somewhat longer. The reaction then proceeds uniformly according to a monomolecular law,

$$-\frac{dc}{dt} = Kc$$

until about 25 molecules of hydrochloric acid per molecule of aluminium chloride had been evolved, after which the reaction ceased. It appeared that the primary formation of the complex $(C_6H_5{\cdot}CH_3)_2Al_2Cl_6$ took place somewhat rapidly, and that the rate of decomposition actually measured was that of the complex :

$$(C_6H_5{\cdot}CH_3)C_6H_5{\cdot}CH_2ClAlCl_3 \rightleftarrows AlCl_3 + C_{14}H_{14} + HCl.$$

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[1] *J. Chem. Soc.*, 1903, **83**, 1470.

Aluminium chloride is thus a true catalyst, but is removed from the sphere of action by a great excess of the hydrocarbon produced. Ferric chloride requires a still greater excess of hydrocarbon to effect its removal.

Steele's investigations on the catalytic activity of the anhydrous chlorides of aluminium and iron on the condensation of toluene and benzoyl chloride yielded somewhat different results.

With a molecular ratio $AlCl_3 : C_6H_5 \cdot CO \cdot Cl$ varying from 0·65 : 1 to 1·3 : 1, the evolution of hydrochloric acid was constant for the first ten minutes. Subsequently it followed the monomolecular law:

$$-\frac{dc}{dt} = Kc$$

for a short period and finally ceased.

With a ratio 2·3 : 1 the ratio of decomposition approximates to that of a bimolecular decomposition

$$-\frac{dc}{dt} = Kc^2.$$

These results are explicable on the assumption that during the first ten minutes the complex was present in excess of its solubility, *i.e.*, the concentration in the solution of the decomposing complex did not alter for this period and consequently

$$-\frac{dc}{dt} = K,$$

or the rate of evolution of hydrogen chloride would be constant. Subsequently, in the presence of small amounts of catalyst, decomposition of the complex proceeded in the normal manner, the aluminium chloride being removed molecule for molecule by the reaction product, the ketone $C_6H_5 \cdot CO \cdot CH_2 \cdot C_6H_5$. In the presence of relatively large amounts of aluminium chloride, it must be assumed that the toluene will also form a complex with the catalyst and that the rate of interaction of two aluminium chloride complexes is being measured:

$$(C_6H_5 \cdot CO \cdot Cl \cdot AlCl_3) + (C_6H_5 \cdot CH_3 \cdot AlCl_3).$$

It will be noted that in this case the catalyst is removed molecule for molecule by the reaction products, whilst in the case of hydrocarbon synthesis the catalyst is only removed by a large excess of the product of the reaction. Goldschmidt and Larsen[1] showed that the condensation of benzyl chloride and anisol was a reaction of the first order and confirmed Steele's observation as to the purely catalytic function of the aluminium chloride.

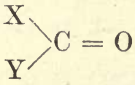
That aluminium chloride can form fairly stable complexes with hydrocarbons, as was suggested by Steele, has been shown to be the case by the researches of Gustavin,[2] who has isolated definite compounds such as $C_6H_6{\cdot}Al_2Cl_6$.

Another application of the catalytic activity of the halides of the elements iron, aluminium, and copper is found in the Sandmeyer reaction, in which the halides of copper are utilised to effect the elimination of nitrogen from diazo-compounds, thus:

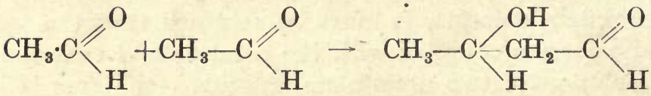
$$C_6H_5{\cdot}N_2Cl + Cu_2Cl_2 = C_6H_5Cl + N_2 + Cu_2Cl_2.$$
$$C_6H_5{\cdot}N_2Cl + Cu_2Br_2 = C_6H_5Br + N_2 + Cu_2BrCl.$$

ALDEHYDE CONDENSATIONS

The aldol condensation.—The condensation of aldehydes and other reactive compounds containing the grouping



where X and Y are hydrocarbon radicles whilst one may be a hydrogen atom, was first investigated by Wurtz,[3] who showed that acetaldehyde, on standing, slowly polymerised into aldol. This condensation can be catalytically hastened by the addition of small quantities of alkali, such as caustic soda or potassium carbonate, or of acids, such as hydrochloric acid:



Hydroxybutyraldehyde.

At somewhat more elevated temperatures, and in the presence

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[1] *Zeitsch. physikal. Chem.*, 1904, **48**, 430.

[2] *Compt. rend.*, 1903, **136**, 1065; 1905, **140**, 940.

[3] *Ibid.*, 1872, **74**, 1361.

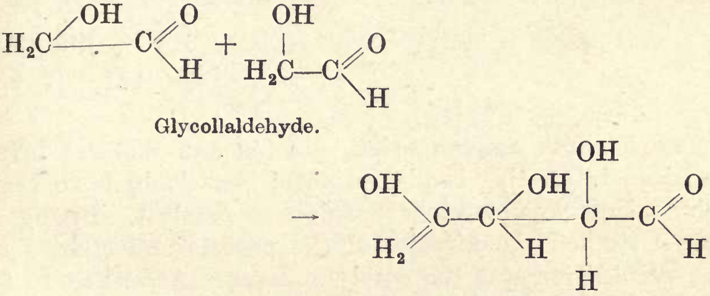
of certain catalysts, especially dehydrating agents such as sulphuric acid, zinc chloride, or acetic anhydride, the aldol condensation product loses water to form a crotonaldehyde condensation product, thus :

$$CH_3{\cdot}C\begin{smallmatrix}OH\\ H\end{smallmatrix} - CH_2{\cdot}C\begin{smallmatrix}O\\ H\end{smallmatrix} \longrightarrow \underset{H}{CH_3{\cdot}C} = CH{\cdot}C\begin{smallmatrix}O\\ H\end{smallmatrix} + H_2O\ ,$$

Crotonaldehyde.

Bakelites, being products of the condensation of formaldehyde and phenols and now extensively used for electrical insulation purposes, are the result of such a series of aldol and crotonaldehyde condensations.

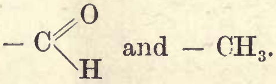
Claisen[1] has made extensive use of dilute caustic soda as catalytic agent in this reaction. Thus synthesis of erythrose from glycollic aldehyde proceeds smoothly in 10 per cent. caustic soda solution :



Glycollaldehyde.

Erythrose.

Aldehydic and crotonaldehydic condensation may of course continue if the aldol condensation product still contains the groupings



$$-C\begin{smallmatrix}O\\ H\end{smallmatrix} \text{ and } -CH_3.$$

Thus, aldehyde resins obtained on boiling acetaldehyde with potash are doubtless of this character. Einhorn and Diehl[2] isolated two products of condensation from benzaldehyde and acetaldehyde :

$C_6H_5{\cdot}CHO + CH_3{\cdot}CHO \rightarrow C_6H_5{\cdot}CH{:}CH{\cdot}CHO + H_2O$

$C_6H_5{\cdot}CH{:}CH{\cdot}CHO + CH_3{\cdot}CHO \rightarrow C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CHO.$

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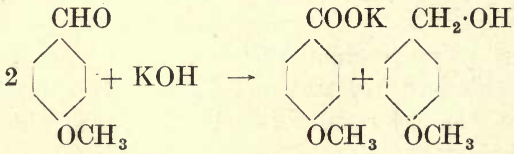
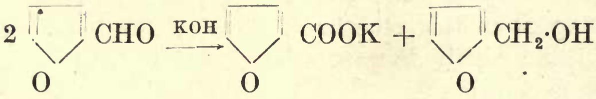
[1] *Ber.*, 1881, **14**, 2471.

[2] *Ibid.*, 1885, **18**, 2370 ; Cohen, " Organic Chemistry," p. 275.

With the higher aliphatic aldehydes or with the aldehydic grouping attached to an electro-negative cyclic nucleus such as the benzene, pyridine, or furfurane ring, the alkali no longer acts as a simple catalyst but serves as a base, forming, as shown by Cannizzaro, the sodium or potassium salt of the respective acid and the corresponding alcohol, thus :



Anisic aldehyde.

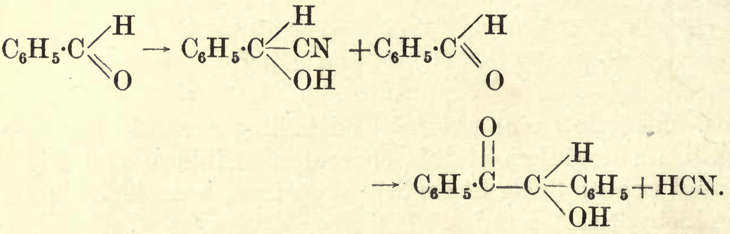


Furfurol.

$$(CH_3)_2CH\cdot CH_2\cdot CHO \xrightarrow{Ca(OH_2)} \{(CH_3)_2{:}CH\cdot CH_2\cdot COO\}_2\cdot Ca + (CH_3)_2CH\cdot CH_2\cdot CH_2\cdot OH$$

Isovaleric aldehyde.

The benzoin condensation.—Liebig and Wöhler[1] investigated an interesting condensation of benzaldehyde to bezoin, using alcoholic potassium cyanide as catalyst. Bredig and Stern[2] studied the kinetics of the process and showed that the cyanide ion was the catalytic agent. According to Lapworth,[3] an intermediate compound, benzaldehyde cyanhydrin, is formed, which subsequently condenses with another molecule of benzaldehyde with the elimination of hydrogen cyanide :



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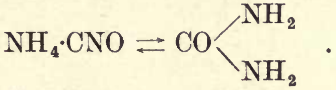
[1] *Annalen*, 1832, **3**, 276.

[2] *Zeitsch. physikal. Chem.*, 1905, **50**, 513.

[3] *J. Chem. Soc.*, 1903, **83**, 995.

CATALYTIC CHANGES OF DYNAMIC ISOMERIDES

Many cases of tautomeric changes are influenced by the presence of certain catalytic agents. There appears little doubt that, on the establishment of a true equilibrium, both forms of the tautomeric substance will be present, but in cases of pseudomeric substances (*e.g.*, the lactam and lactim forms of isatin), one form is usually practically absent, or present in extremely small quantities. This, however, must be attributed to the fact that under the conditions of the experiment the equilibrium has been shifted very far in one direction. Thus, in the usual urea–ammonium cyanate equilibrium, 95 per cent. of urea represents the equilibrium amount under normal conditions :



$$NH_4{\cdot}CNO \rightleftharpoons CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. .$$

5 per cent. 95 per cent.

In the case of many allelotropic modifications in which at equilibrium the two forms are present in determinable quantities, each form can be isolated in the pure state and its rate of conversion be determined, provided that the reaction velocity of the re-establishment of equilibrium be not extremely rapid.

Much confusion in the past was caused in the classification of types of dynamic isomeric changes owing to the fact that either the intraconvertible forms were extremely labile in the pure state and could frequently not be isolated as such, or, on the other hand, they were very stable and only proceeded to form an equilibrium mixture with difficulty. It is evident that these differences are merely one of degree.[1] Lowry has noted that in cases of dynamic isomerism where two radicals are interchanged and when neither radical can be split off as an ion in either compound, the catalytic agent is invariably an acid or an acidic substance. Thus, in fumaric–

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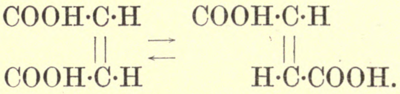
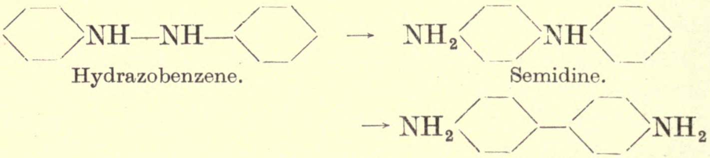
[1] See Lowry, *Brit. Assoc. Reports,* 1904, p. 193.

maleic acid equilibrium hydrobromic acid is the most effective catalyst:



$$\begin{array}{c}\mathrm{COOH\cdot C\cdot H}\\ \|\\ \mathrm{COOH\cdot C\cdot H}\end{array} \rightleftarrows \begin{array}{c}\mathrm{COOH\cdot C\cdot H}\\ \|\\ \mathrm{H\cdot C\cdot COOH.}\end{array}$$

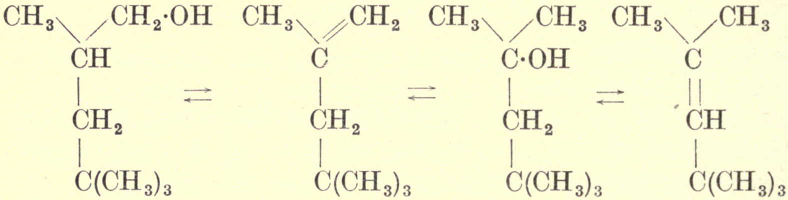
In the benzidine conversion mineral acids are invariably used:[1]



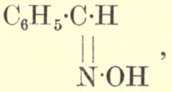
Hydrazobenzene. Semidine.

Benzidine.

Of historic interest is Butlerow's investigation[2] of the action of trimethyl carbinol in dilute sulphuric acid, a quaternary equilibrium between the two isodibutylenes and their respective alcohols being established:

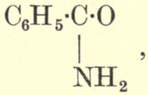


In the Beckmann change,[3] the benzaldoximes,



$$\begin{array}{c}\mathrm{C_6H_5\cdot C\cdot H}\\ \|\\ \mathrm{N\cdot OH}\end{array},$$

are converted into the acid amides,



$$\begin{array}{c}\mathrm{C_6H_5\cdot C\cdot O}\\ |\\ \mathrm{NH_2}\end{array},$$

by a trace of hydrochloric acid or phosphorus oxychloride.

The use of many similar acid catalysts is also to be noticed

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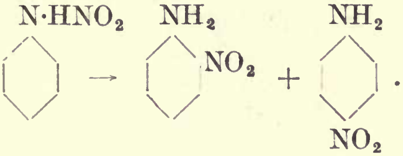
[1] See Jacobsen, *Annalen*, 1899, **303**, 290, and Goldschmidt, *Ber.*, 1889, **29**, 1369.

[2] *Annalen*, 1877, **189**, 76.

[3] *Ber.*, 1889, **22**, 1537.

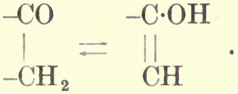
in the transference of groups from the side chain to the aromatic nucleus. Thus, Bamberger[1] obtained the transference of a nitro-group by the addition of a small quantity of mineral acid :



Similar transferences of one or more methyl groups have been obtained by Hofmann and Martius,[2] the sulphonic group by Hindermann,[3] as well as the $-NO$, and $-CH_3\cdot CO$ groupings by different investigators.

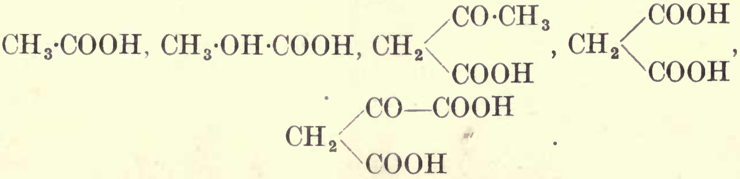
In those cases in which a single radical is transferred from one position to another and in which the radical may be capable of acting as an ion in both forms or at least in one form, the catalytic agent is, according to Lowry, invariably an alkaline substance.

The most important cases of this class of dynamic isomeric change are the keto-enol modifications in which the isomers differ only in the position of a labile hydrogen atom :



$$\begin{matrix} -CO \\ | \\ -CH_2 \end{matrix} \rightleftharpoons \begin{matrix} -C\cdot OH \\ \| \\ CH \end{matrix} .$$

The reactivity of a hydrogen atom attached to a carbon atom increases as the balance between the electro-positive and electro-negative groupings in the molecule becomes less. Thus, in the following compounds the activity or lability of the hydrogen becomes greater owing to the insertion of more electro-negative groupings in the molecule.



$$CH_3\cdot COOH,\ CH_3\cdot OH\cdot COOH,\ CH_2\begin{matrix} \diagup CO\cdot CH_3 \\ \diagdown COOH \end{matrix},\ CH_2\begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix},$$

$$CH_2\begin{matrix} \diagup CO-COOH \\ \diagdown COOH \end{matrix} .$$

In malonic acid both hydrogens of the nucleus $>CH_2$ have already become labile, and are even capable of replacement

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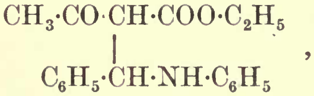
[1] *Ber.*, 1897, **30**, 1288. [2] *Ibid.*, 1878, **4**, 742. [3] *Ibid.*, 1897, **30**, 654.

by sodium. Acetoacetic ester has also two labile hydrogen atoms, but only one sodium salt is known.

Acetoacetic ester exists both in the keto and enol forms in solution. Thus, it shows reactivity towards both ketone reagents, such as phenylhydrazine and to enol reagents, *e.g.*, phenylcarbimide or ferric chloride. By the addition of such substances the equilibrium is shifted and complete conversion can finally ensue if sufficient of the reagent be added, although in the case of ferric chloride the complex Fe (enol)$_3$[$FeCl_3 + 3$ enol form $\rightleftarrows$ Fe (enol)$_3 + 3HCl$] is formed to such a slight extent that the equilibrium is barely affected.

The solvent itself may influence the equilibrium by combining with one or both of the isomeric forms. In these cases also the change from ketonic to enolic form is accelerated by the addition of small quantities of bases.

The work of Schiff on the condensation of acetoacetic ester and benzalaniline[1] has, however, indicated that this catalytic activity of bases in the keto-enol conversion leads to somewhat unexpected results. He noted that complete conversion of the keto form,



$$\begin{array}{c} CH_3\cdot CO\cdot CH\cdot COO\cdot C_2H_5 \\ | \\ C_6H_5\cdot CH\cdot NH\cdot C_6H_5 \end{array},$$

to the enol form could be obtained by the addition of a trace of sodium ethoxide to the reagent, whilst the reverse change could likewise be accomplished by the addition of piperidine. Evidently the action is not purely catalytic, since the equilibrium is disturbed; Lowry has assumed[2] that the sodium ethoxide forms an additive compound with the enol form of acetoacetic ester, which then interacts with the benzaniline and liberates the sodium ethoxide. In this way the enol form of acetoacetic ester is continuously removed from the sphere of action and keto-enol conversion takes place to re-establish equilibrium.

The nitro-bodies.—Victor Meyer first indicated the tautomeric nature of nitro-derivatives by isolating methyl nitrite, $CH_3\cdot O\cdot NO$ (b.p. $-16°$), and nitromethane, CH_3NO_2 (b.p. 110°), by the interaction of methyl iodide and silver or potassium

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[1] *Ber.*, 1898, **31**, 205; 1899, **32**, 332.

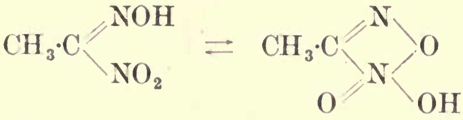
[2] *J. Chem. Soc.*, 1899, **75**, 241.

nitrite. Kolbe's experiments on the solubilities of various halogen-substituted nitro-bodies conclusively showed that solubility in alkali was conditioned by the presence of a labile hydrogen atom. Thus, all derivatives of the type $\rangle\mathrm{CHNO_2}$ were soluble, whilst those of type $-\!\rangle\mathrm{CNO_2}$ were insoluble. Hantzsch and Schultze[1] showed that the two isomers in the case of phenol nitromethane could be transformed one into the other, equilibrium between the two forms being assumed to exist:

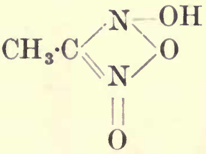
$$\underset{\text{Phenol nitromethane.}}{\mathrm{C_6H_5{\cdot}CH_2{\cdot}NO_2}} \rightleftharpoons \underset{\psi\text{-Nitrotoluene.}}{\mathrm{C_6H_5{\cdot}CH{:}NO{\cdot}OH}}.$$

ψ-Nitrotoluene is a strong acid and an electrolyte, whilst phenylnitromethane is an oil and a non-electrolyte. The change of the oil into the conducting form is accelerated by the presence of bases, whilst the reverse change is influenced by the addition of acids; in alcoholic solutions also, the ψ-nitrotoluene, which can be precipitated in a pure form from its sodium salt, is gradually transformed to the phenylnitromethane form. Similar results are obtained with nitromethane. Thus, on the addition of baryta water to nitromethane the period of time required for the tautomeric change to complete itself with formation of the barium salt exceeds fifteen minutes.

Hantzsch's investigations on these forms of ionic isomerism in pseudo-acids were extended to the nitrolic acids:

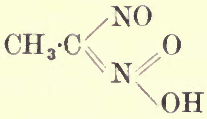


He was successful in isolating (by neutralisation with caustic soda) the intermediate forms:[2]



Red salt.

and



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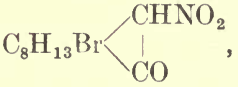
[1] *Ber.*, 1896, **29**, 699; 1899, **32**, 575.

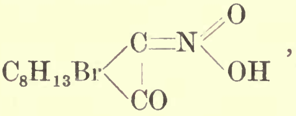
[2] See also Hantzsch's investigations on ψ-ammonium bases, *Ber.*, 1899, **32**, 594; 1900, **33**, 278.

Lowry and E. Armstrong[1] and Lowry[2] have followed the tautomeric changes of the isomeric nitro- and π-bromonitrocamphor by means of the change in optical rotatory power. The normal form of π-bromonitrocamphor,



$$C_8H_{13}Br{<}\begin{matrix}CHNO_2\\ |\\ CO\end{matrix},$$

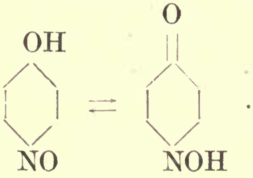
has a rotatory power $[\alpha]_D - 51°$ whilst the ψ-form,



$$C_8H_{13}Br{<}\begin{matrix}C{=}N{<}\begin{matrix}O\\ OH\end{matrix}\\ |\\ CO\end{matrix},$$

has a value $[\alpha]_D + 188°$.

Similar tautomeric changes are observed in the case of nitrophenol and quinonemonoxime,



A well-investigated case of catalytic influence on the migration of an atom within the molecule is to be found in the catalytic conversion of acetochloroaniline to *p*-chloroacetanilide,

$$C_6H_5{\cdot}NCl(CO{\cdot}CH_3) \longrightarrow ClC_6H_4{\cdot}NH(CO{\cdot}CH_3).$$

The reaction is of importance in the consideration of the question of reactivity of various agents with anilines and anilides. Blanksma[3] measured the velocity with which this change occurs in presence of hydrochloric acid, and showed that the reaction was apparently monomolecular, but that, by doubling the acid concentration, the velocity constant of the reaction was increased fourfold. With sulphuric acid, it was impossible to obtain constancy in the velocity determinations. Light was shown to possess a marked accelerating action.

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[1] *J. Chem. Soc.*, 1903, **83**, 1314.

[2] *Ibid.*, 1899, **75**, 235.

[3] *Proc. K. Akad. Wetensch. Amsterdam*, 1902, **5**, 178, 359.

Orton[1] and Orton and Jones[2] showed in the course of experiments on the interaction of various acids with chloroamines that chlorine could always be detected when hydrochloric acid was present, but not when one of the other acids was present. This fact led, on further investigation, to the conclusion that an equilibrium,

$$C_6H_5{\cdot}NHAc + Cl_2 \rightleftharpoons C_6H_5{\cdot}NClAc + HCl,$$

is always rapidly established and is then slowly disturbed by the formation of the *p*-chloroacetanilide, by interaction of chlorine and acetanilide, the equilibrium being expressed by the equation :—

$$K[C_{\text{anilide}}]\,[C_{\text{chlorine}}] = [C_{\text{chloroamine}}]\,[C_{\text{HCl}}]$$

The reaction, therefore, would be proportional to the concentration of the acetochloroanilide and consequently of the first order as found by Blanksma.

Acree and Johnson[3] assume, in explanation of the reaction mechanism, that a compound between the acetochloroamine and hydrochloric acid is formed which is dissociated, the undissociated fraction, however, being slowly changed over into *p*-chloroacetanilide with simultaneous liberation of free hydrochloric acid.

Rivett[4] showed that the reaction velocity constant K, in varying concentrations of hydrochloric acid, C, was expressible by the equation :—

$$K = (l - a)\,C\,(A + B\,a\,C)$$

where a was the degree of dissociation, and A and B were specific constants. Rivett was unable to find catalytic acceleration in the presence of other acids. Interpreting his equation in the light of Acree and Johnson's views, Rivett[5] suggested that this would imply that the undissociated hydrochloric acid molecule plays the principal part in the formation of the intermediate compound and that the ions exert an accelerating influence on the reaction. Rivett further investigated the action of neutral chlorides on the change in presence of hydrochloric acid. The usual accelerating influence of neutral

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[1] *Proc. Roy. Soc.*, 1902, **71**, 156.

[2] *J. Chem. Soc.*, 1909, **95**, 1456.

[3] *Amer. Chem. J.*, 1907, **38**, 265.

[4] *Zeitsch. physikal. Chem.*, 1913, **82**, 201.

[5] *Ibid.*, 1913, **85**, 113.

salts was observed, and could be stated in the form of an equation of the form:

$$K = (\mathrm{HCl})\{0{\cdot}050 + a(\mathrm{H}) + b(\mathrm{Cl}') + d(M')\}$$

where a, b, and d are specific constants, dependent only on the nature of the particular ions present. Ammonium chloride constituted an exceptional case, the reaction at the outset in presence of varying quantities of salt going much more slowly, at the end, however, with much greater rapidity than in the pure acid alone. It was shown that such a result was in accord with the viewpoint as to mechanism put forward by Orton and Jones.

The cyanides.—Attention may be directed to the somewhat complex case of the cyanide–isocyanide tautomeric substances. It is well known that the production of either cyanide or isocyanide can be controlled by utilising the potassium or silver salt of hydrocyanic acid for interaction with an alkyl iodide, thus:

$$\mathrm{CH_3I}\begin{array}{lcl} \mathrm{KCN} & \rightarrow & \mathrm{CH_3{\cdot}CN} \\ \mathrm{AgCN} & \rightarrow & \mathrm{CH_3{\cdot}NC} \end{array}$$

We may assume that the alkyl cyanides and isocyanides themselves are tautomeric and that the production of cyanide by the use of the potassium salt is due to the necessity of heating the reacting substances, KCN and CH_3I, to a higher temperature than for the silver salt.[1] It seems probable, however, that the difference in the two reactions is more fundamental.

Hydrocyanic acid itself probably possesses the structure $\mathrm{H{\cdot}C}\vdots\mathrm{N}$, since it is easily hydrolysed by alkalies and both in refractive power and physiological activity is more akin to the alkyl cyanides. All the metallic cyanides, however, resemble the alkyl isocyanides both in their reactivity to form double compounds and in their physiological effects. Thus we must regard the constitution of both silver and potassium salts as similar and of the form $\mathrm{K{\cdot}N}\vdots\mathrm{C}$ and $\mathrm{AgN}\vdots\mathrm{C}$. With Nef, we may regard the formation of cyanide and isocyanides as determined by the influence of the difference in the electrical character of the metallic ion and the formation

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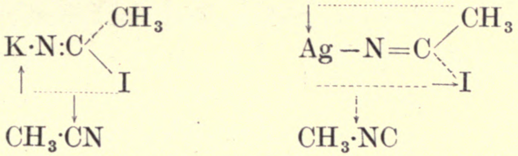
[1] Wade, *J. Chem. Soc.*, 1902, **81**, 603.

of the salts to take place through the mechanism of additive products :



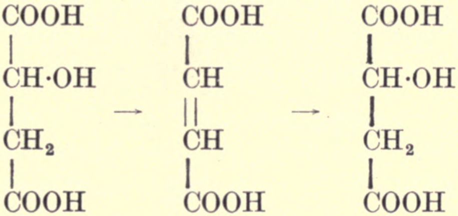
Thus, potassium must be regarded as more electropositive than both CH_3 and CH_3I, whilst silver on this view is comparable with CH_3.

The elements potassium and silver, in the ionic form, consequently exert selective action on account of their differences in electrical absorptive capacities.

RACEMISATION AND MUTAROTATION

Racemisation.—In several well-known examples of racemisation of optically active forms of compounds, certain catalysts accelerate the conversion and are frequently utilised isntead of the more usual method of elevating the temperature; thus, although active tartaric acid when heated to 170° *per se* is converted into the racemic and meso-forms, conversion into the racemic form can be produced at a lower temperature by the addition of aluminium oxide.

Active malic acid is racemised by heating to 104° with water. These changes are generally attributed to the elimination and subsequent addition of water, thus :



$$\begin{array}{c} COOH \\ | \\ CH\cdot OH \\ | \\ CH_2 \\ | \\ COOH \end{array} \rightarrow \begin{array}{c} COOH \\ | \\ CH \\ \| \\ CH \\ | \\ COOH \end{array} \rightarrow \begin{array}{c} COOH \\ | \\ CH\cdot OH \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

Active malic. Inactive fumaric. Inactive malic.

Leucine (α-amidocaproic acid) and hyoscyamine are particularly sensitive to the presence of small quantities of hydroxyl ions, and the latter compound has been utilised for measuring the strength of bases by following polarimetrically the rate of racemisation.[1]

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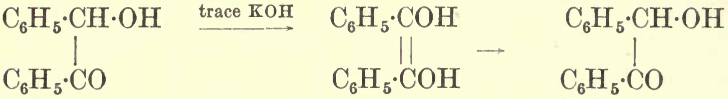
[1] Bredig and Will, *Ber.*, 1888, **21**, 2777.

A similar result was obtained by Wren[1] in the racemisation of *l*-benzoin by means of a trace of caustic potash. He was successful in isolating the intermediary enol form :



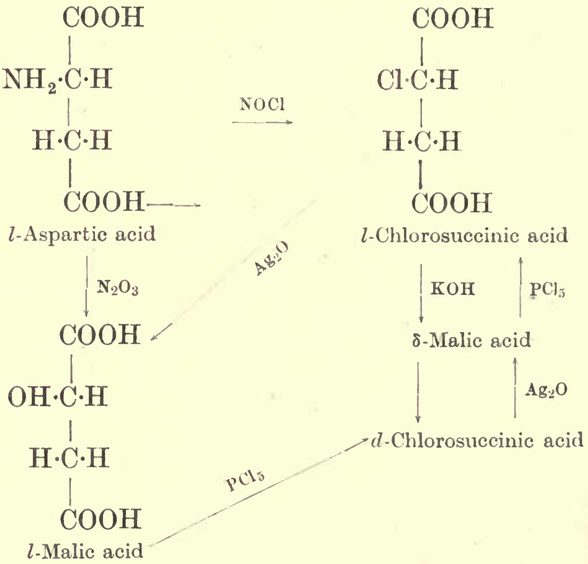
$$\begin{array}{c} C_6H_5{\cdot}CH{\cdot}OH \\ | \\ C_6H_5{\cdot}CO \end{array} \xrightarrow{\text{trace KOH}} \begin{array}{c} C_6H_5{\cdot}COH \\ \| \\ C_6H_5{\cdot}COH \end{array} \longrightarrow \begin{array}{c} C_6H_5{\cdot}CH{\cdot}OH \\ | \\ C_6H_5{\cdot}CO \end{array}$$

l-Benzoin. Inactive.

In the examples cited above attention has been directed to the catalytic activity of traces of alkali, and its activity has been attributed to the formation of unstable intermediary compounds without any stress being laid on the function of the alkali during the process of optical inversion.

In the case of the so-called Walden inversion, however, where the catalyst functions in the chemical reaction itself and not purely in a catalytic capacity, the magnitude and nature of the optical inversion is not independent of the nature of the added catalyst and chemical reactant, but is greatly influenced by it, as will be noted by the following typical examples :

(*a*) The Walden inversion :[2]



In this case, KOH must be considered optically normal and Ag_2O optically abnormal.

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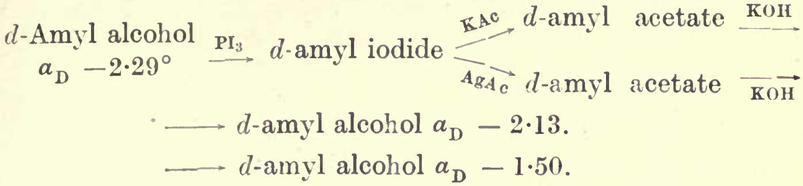
[1] *J. Chem. Soc.*, 1909, **95**, 1583.

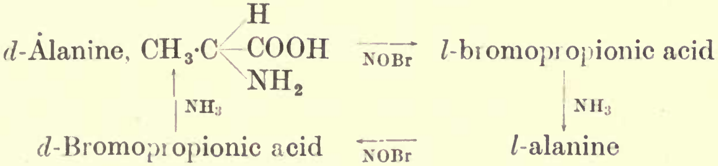
[2] P. Walden, *Ber.*, 1875, **28**, 2766 *et seq.*

(*b*) Marckwald and Nolda's racemisation of amyl alcohol.[1]



In this case racemisation is also caused by the silver salt.

Fischer[2] investigated the racemisation of various amino-acids during chemical change. Thus:



In the case of the ethyl ester of δ-alanine, however, no inversion of sign took place when similarly treated with nitrosyl bromide, hence inversion was caused, not only by the action of the nitrosyl bromide, but also by the presence of the ·COOH grouping.

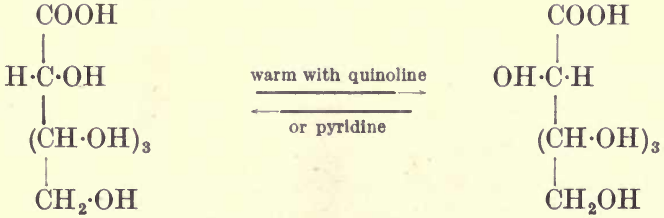
Fischer obtained similar results when silver carbonate was used as hydrolytic and catalytic agent for *a*-halogen-substituted aliphatic acids; racemisation was not obtained when the ·COOH grouping was protected by a polypeptide.

It may be noted that racemisation during chemical reactions of this nature does not take place when the active carbon atom is not in juxtaposition to the carboxyl group, *e.g.*:

$$CH_3{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOH$$

gives no inversion with any of the reagents.

Similar results were obtained by Fischer in his investigations of the acids derived from sugars, *e.g.*:



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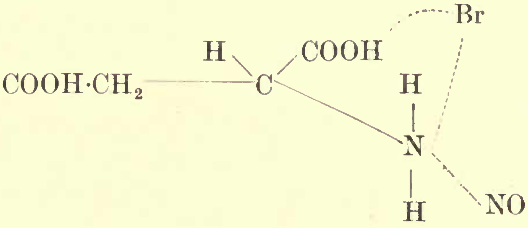
[1] *Ber.*, 1909, 42, 1583.

[2] *Ibid.*, 1907, 40, 409.

Many instances of the Walden inversion have been investigated since Walden's original observations,[1] but the complexity of the problem is made more difficult by the fact that the catalytic activity of the reagent in causing racemisation is frequently masked by its chemical activity. It appears, however, that PCl_5 is always optically normal in its behaviour and nitrosyl bromide always abnormal, silver oxide is generally abnormal, whilst potash, nitrous acid, and ammonia are frequently normal, but many exceptions are found in these latter cases.[2] We may consider the mechanism to be one of addition with subsequent decomposition with or without racemisation; thus in the case of the action of nitrosyl chloride on *l*-aspartic acid, the intermediary complex

$$(COOH{\cdot}CH_2{\cdot}CH{\cdot}NH_2{\cdot}COOH{\cdot}NOCl)$$

is formed, the NOCl being added to the most electro-negative part of the molecule:



It is evident that during the elimination of nitrogen and water the bromine atom is temporarily free. It may, during this period, take up the place occupied by the ·COOH grouping, which must then revert to the space left by the eliminated nitrogen atom.

Mutarotation—Very similar to these changes in optical activity on the addition of certain catalysts to organic substances containing an asymmetric carbon atom in juxtaposition to an electro-negative grouping such as the carboxyl group is the behaviour of certain sugars on standing in aqueous solution or in a slightly alkaline medium.

Parcus and Tollens[3] tabulated the initial and final specific rotations of the solutions of a number of natural sugars after

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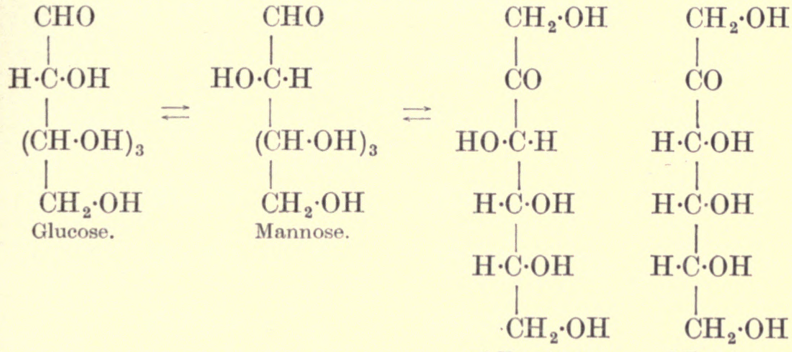
[1] See Frankland's Presidential Address to the Chemical Society, 1908.

[2] See McKenzie and Clough, *J. Chem. Soc.*, 1908, **93**, 811.

[3] *Annalen*, 1890, **287**, 160.

being allowed to stand in an alkaline solution for some hours. For example, *d*-glucose $\alpha_D + 105{\cdot}2°$ sinks to $\alpha_D + 52{\cdot}6°$ after a few hours and remains constant at that figure. Xylose, $\alpha_D + 78{\cdot}6°$, sinks to $\alpha_D + 19{\cdot}2°$, and rhamnose $\alpha_D - 3{\cdot}0°$ rises to $\alpha_D + 9{\cdot}4°$.

Lobry de Bruyn[1] and V. Ekenstein[2] noted the inter-conversion of glucose, mannose and fructose on the addition of a little alkali to one of the sugars :



Glucose. Mannose. *d*-Fructose. *l*-Fructose.

Morrel and Bellars[3] obtained similar results with guanidine, which is nearly as strong a base as caustic soda, but has the advantage of forming crystalline compounds with the sugars which may thus be isolated. These investigators obtained the following values of the velocity coefficients of each change at 37°.

$$\begin{tikzcd}
 & \text{Glucose} \arrow[dr, shift left, "\text{NaOH}"] & \\
\text{Mannose} \arrow[ur, "0{\cdot}00056"] \arrow[dr, "0{\cdot}00005"'] & & \text{Intermediate substance.} \arrow[ul, shift left, "0{\cdot}0015"'] \arrow[dl, shift right, "\text{NaOH}"'] \\
 & \text{Fructose} \arrow[ur, shift right, "0{\cdot}0021"'] &
\end{tikzcd}$$

Tanret[4] isolated three modifications of glucose itself, α-glucose crystallised from cold solutions, $\alpha_D + 105°$; β-glucose from hot solutions, $\alpha_D + 52{\cdot}5°$, and γ-glucose from hot alcohol, $\alpha_D + 22{\cdot}0°$. β-Glucose is in all probability a dynamic isomer of the other varieties.

Both the formation of isomeric glucoses and the conversion of glucose into isomeric sugars may be attributed to the addition of water followed by subsequent dehydration ; we

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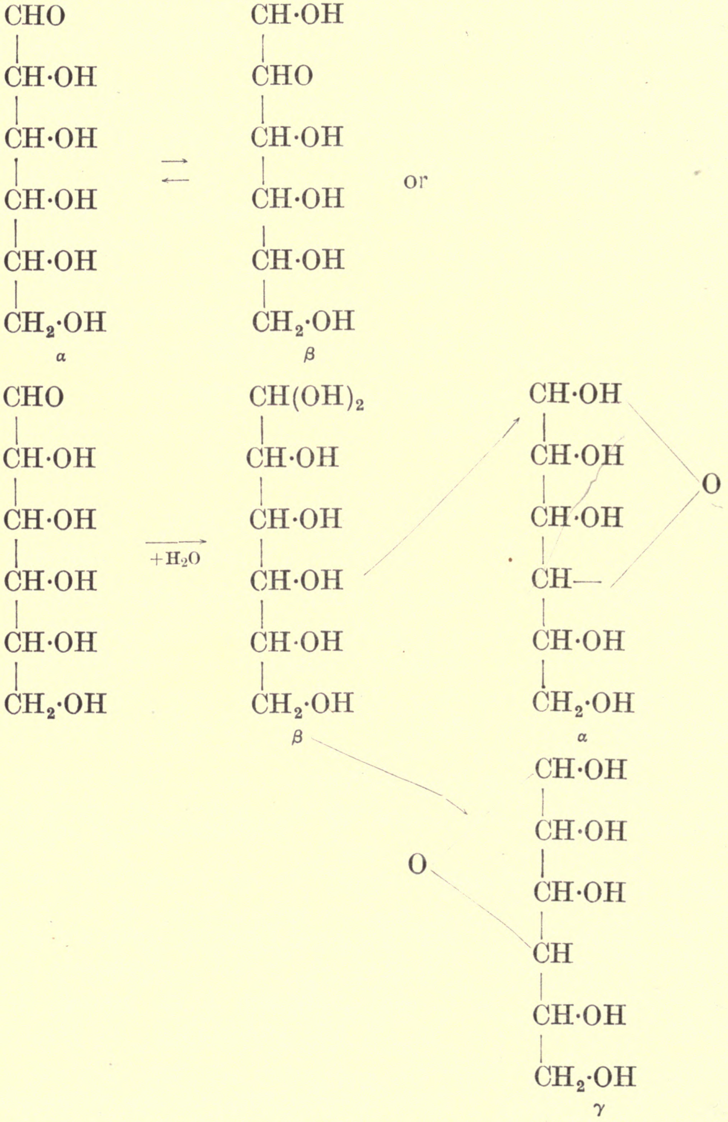
[1] *Rec. trav. chim.*, 1900, **17**, 1.

[2] *Ber.*, 1895, **28**, 3078.

[3] *J. Chem. Soc.*, 1907, **91**, 1010.

[4] *Compt. rend.*, 1895, **120**, 1860.

may consider the formation of the *α*- and *γ*-glucoses to take place by either of the following methods :



From a study of the physical properties[1] of the *α*- and *γ*-fructoses as well as from E. F. Armstrong's experiments

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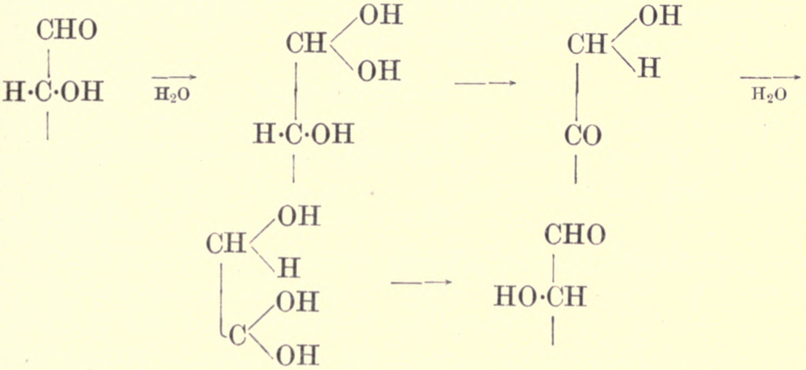
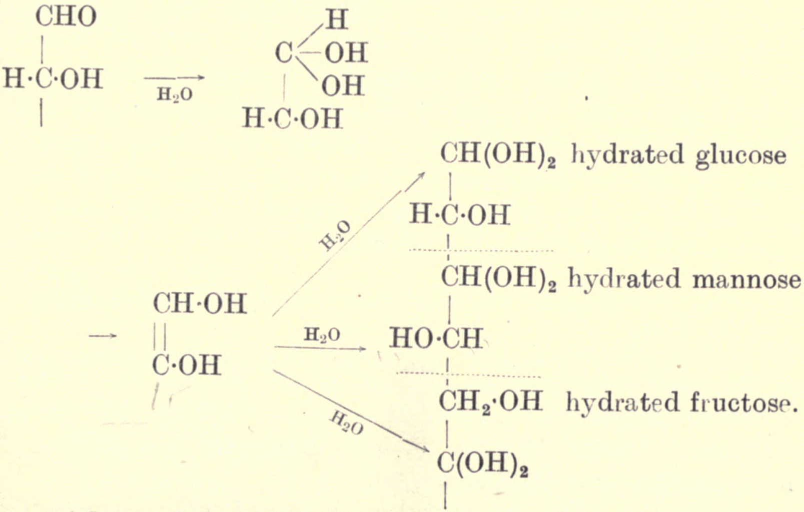
[1] W. H. Perkin, *J. Chem. Soc.*, 1902, **81**, 177 ; Lowry, *ibid.*, 1903, **83**, 1314.

on the hydrolysis of the glucosides,[1] it appears probable that the internal anhydride structure for the glucoses originally proposed by Tollens is more probable than the transference of a hydrogen atom from the first asymmetric carbon atom. The anhydrides of the real hydrated glucose thus exist in two forms, due to the introduction of a new asymmetric carbon atom into the molecule.

The interconversion of glucose to mannose and fructose may be interpreted in a similar manner, thus :



Lowry[2] suggests an alternative scheme in which the hydrated glucose loses water to form an enolic compound from which all the sugars may be derived :



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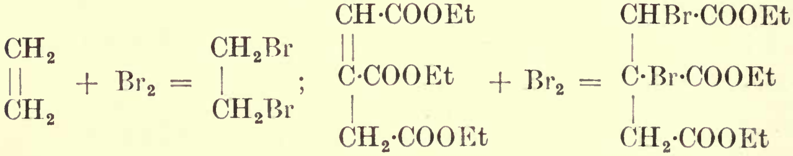
[1] Lowry, *J. Chem. Soc.*, 1903, **83**, 1305.

[2] *Loc. cit.*, 1314.

HALOGENATION

Several catalytic agents are employed for introducing the halogens into organic compounds, of which the most interesting is the agency of direct sunlight or exposure to various forms of radiant energy. The action of bright sunlight on the halogenation of unsaturated hydrocarbons favours the formation of simple additive products, as in the bromination of ethylene or of aconitic ester :



$$\begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} + \mathrm{Br_2} = \begin{matrix}\mathrm{CH_2Br}\\ |\\ \mathrm{CH_2Br}\end{matrix}\;;\quad \begin{matrix}\mathrm{CH\cdot COOEt}\\ \|\\ \mathrm{C\cdot COOEt}\\ |\\ \mathrm{CH_2\cdot COOEt}\end{matrix} + \mathrm{Br_2} = \begin{matrix}\mathrm{CHBr\cdot COOEt}\\ |\\ \mathrm{C\cdot Br\cdot COOEt}\\ |\\ \mathrm{CH_2\cdot COOEt}\end{matrix}$$

or in the chlorination of benzene :

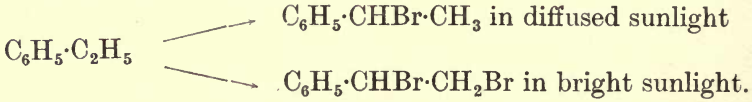
$$\mathrm{C_6H_6 + 3Cl_2 = C_6H_6Cl_6}$$

in which hexachlorohexamethylene is formed, but which is unstable and rearranges according to the equation :

$$\mathrm{C_6H_6Cl_6 = C_6H_3Cl_3 + 3HCl}$$

In the dark, substitution of a halogen atom for a hydrogen atom usually results.

In the case of the fatty aromatic hydrocarbons and their derivatives, direct sunlight favours the halogenation of the side chain and not the nucleus, a similar result being obtained when the process is conducted at the boiling point. Substitution in the nucleus results from halogenation in the dark, as exemplified in the following reactions :



$$\mathrm{C_6H_5\cdot C_2H_5}\begin{matrix}\nearrow \mathrm{C_6H_5\cdot CHBr\cdot CH_3}\text{ in diffused sunlight}\\ \searrow \mathrm{C_6H_5\cdot CHBr\cdot CH_2Br}\text{ in bright sunlight.}\end{matrix}$$

Several elements or their anhydrous chlorides, the latter frequently formed *in situ*, likewise accelerate the process of halogenation to a marked degree.

Iodine has been successfully employed for processes of chlorination and of bromination.[1] Substitution in the nucleus usually results when iodine is used as catalyst in the halogenation of aromatic substances. Its function as a halogen carrier is probably dependent on two factors, first, the formation of a monohalide, for example, ICl or IBr, which in virtue of its unsymmetrical character, as opposed to Cl·Cl or Br·Br, is capable of reacting with unsaturated linkages; secondly, the power of oscillation of the halides of iodine between the two stages of halogenation,

$$ICl + Cl_2 = ICl_3,$$

thus exhibiting a marked case of carrier action. In a later chapter on the action of radiant energy in promoting chemical change the further action of iodine in removing the negative catalyst, oxygen, from a system undergoing halogenation is emphasised.

Various varieties of charcoal[2] rapidly effect the combination of hydrogen and chlorine. During the last few years, wood charcoal has been employed, as suggested by Schiel,[3] in the preparation of the poison gas, carbonyl chloride, from chlorine and carbon monoxide. In this synthesis, it is interesting to note that hydrogen chloride is said to be a negative catalyst, and the preparation of dry carbon monoxide on a large scale offered at first considerable technical difficulties, which were finally overcome by burning charcoal in oxygen and diluting the gas with carbon dioxide in order to prevent undue elevation of the temperature. Ethyl chloride, also, can be progressively and quantitatively converted into hexachloroethane by chlorination at 350° in presence of blood charcoal.

Sulphur and sulphur chloride have been employed as catalysts for the chlorination of acetic acid to yield the monochloro-derivative.[4]

Phosphorus pentachloride generally undergoes partial or

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[1] Müller, *Jahresber. Ges. vaterl. Kultur*, 1862, p. 414; Kraft, *Ber.*, 1877, **10**, 801; Klasson, *ibid.*, 1887, **20**, 2382; Bruner and Dluska, *Bull. Acad. Sci. Cracow*, 1907, p. 691.

[2] Paternò, *Gazzetta*, 1878, **8**, 233.

[3] *Jahresber. Ges. vaterl. Kultur*, 1864, p. 309.

[4] Auger and Behal, *Bull. Soc. chim.*, 1889, **2**, 145; Russanoff, *Ber.*, 1892, **25**, 334.

complete conversion to the oxychloride when present in the chlorination of aldehydes and ketones.

Of the metallic halides, ferric chloride and bromide are the most active catalysts.[1] Thus, an almost quantitative yield of chloral may be obtained from alcohol in the presence of ferric chloride, whilst bromination of benzene to monobromobenzene, a reaction which proceeds slowly in the dark with but a 50 per cent. conversion, proceeds smoothly with ferric bromide to completion. Iodination in the nucleus cannot be accomplished directly without the aid of catalytic agents such as ferric chloride, mercuric oxide, or iodic acid.[2]

As in the Friedel-Crafts' reaction, aluminium chloride exerts a catalytic activity equal to that of ferric chloride in processes of halogenation.[3]

Aronheim[4] has shown that molybdenum pentachloride is an efficient catalyst for the halogenation of aromatic compounds, but is perfectly inert when aliphatic substances are employed.

Antimony pentachloride,[5] tin tetrachloride,[6] and the halides of zinc[7] and mercury[8] have all been shown to exert a catalytic activity, but with the exception of antimony pentachloride. which is more active than iodine, their application has been restricted merely to special investigations.

Attention may be directed to the remarkable catalytic activity exhibited by camphor and anhydrous formic acid in promoting the combination of sulphur dioxide and chlorine. If camphor be saturated with sulphur dioxide and dry chlorine be then passed into the solution, sulphuryl chloride is rapidly and quantitatively obtained. In the absence of catalyst, reaction only occurs at red heat.

THEORETICAL DISCUSSION

It is a difficult matter to formulate any satisfactory theory to serve as an explanation for the actual mechanism of those

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[1] Schenfelen, *Annalen*, 1885, **231**, 164.

[2] Lothar Meyer, *Annalen*, 1885, **231**, 195.

[3] Leroy, *Bull. Soc. chim.*, 1887, **48**, 210.

[4] *Ber.*, 1875, **8**, 1400 ; 1876, **9**, 1788.

[5] Ruoff, *ibid.*, 1876, **9**, 1486.

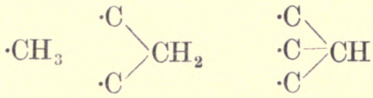
[6] Petricou, *Bull. Soc. chim.*, 1890, **3**, 187.

[7] Schiaparelli, *Gazzetta*, 1882, **11**, 70.

[8] Lazarew, *J. Russ. Phys. Chem. Soc.*, 1890, **22**, 287.

reactions in organic chemistry which are markedly susceptible to catalytic influences, since our knowledge not only of the conditions governing catalytic susceptibility but also those of chemical activity for any specific atom in the molecule is distinctly scanty.

From a comparison of the reactivities of a hydrogen atom in the groups



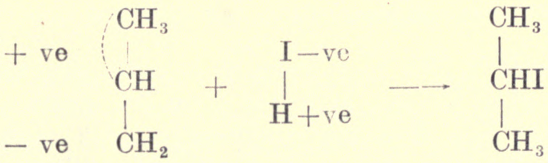
it appears that the reactivity is influenced by, if not dependent on, the relative number and proximity of electro-positive and electro-negative groupings in the molecule; well-known examples are found in the high reactivity of the tertiary alkyl iodides which progressively sinks in the case of the secondary and primary iodides.

The point of attack in a molecule is generally the weakest point where an excess of electro-negative groups over positive ones are to be found, and the tendency is for these electro-negative groups to be removed by the reaction; thus in the oxidation of ethyl alcohol oxidation commences in the

$$\cdot CH_2\cdot OH$$

and not in the $\cdot CH_3$ grouping.

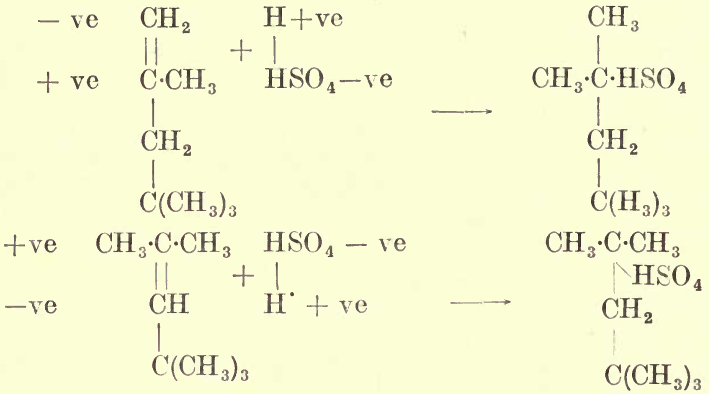
When additive compounds are formed we must also assume that there will be a tendency for internal electric compensation, thus:



$$\begin{array}{ccccccc} & CH_3 & & & & & CH_3 \\ +\text{ ve} & | & & I-\text{ve} & & & | \\ & CH & + & | & \longrightarrow & & CHI \\ & | & & H+\text{ve} & & & | \\ -\text{ ve} & CH_2 & & & & & CH_3 \end{array}$$

or in the case of acrylic acid, $CH_2{:}CH\cdot COOH + HI \rightarrow CH_2I\cdot CH_2\cdot COOH$, since the grouping $:CH\cdot COOH$ is more electro-negative than the grouping $:CH\cdot H$.

In the case of the isobutylenes already discussed we may expect the addition of sulphuric acid to take place even in dilute solutions, owing to the great electro-positive and -negative differences between the reactants :



$$\begin{array}{lllll} -\text{ve} & \mathrm{CH_2} & \mathrm{H}+\text{ve} & & \mathrm{CH_3} \\ & \| \quad + & | & & | \\ +\text{ve} & \mathrm{C{\cdot}CH_3} & \mathrm{HSO_4}-\text{ve} & & \mathrm{CH_3{\cdot}C{\cdot}HSO_4} \\ & | & & \longrightarrow & | \\ & \mathrm{CH_2} & & & \mathrm{CH_2} \\ & | & & & | \\ & \mathrm{C(CH_3)_3} & & & \mathrm{C(H_3)_3} \end{array}$$

$$\begin{array}{lllll} +\text{ve} & \mathrm{CH_3{\cdot}C{\cdot}CH_3} & \mathrm{HSO_4}-\text{ve} & & \mathrm{CH_3{\cdot}C{\cdot}CH_3} \\ & \quad \| \quad + & | & & \quad |\diagdown \mathrm{HSO_4} \\ -\text{ve} & \quad \mathrm{CH} & \mathrm{H^{\cdot}}+\text{ve} & \longrightarrow & \quad \mathrm{CH_2} \\ & \quad | & & & \quad | \\ & \quad \mathrm{C(CH_3)_3} & & & \quad \mathrm{C(CH_3)_3} \end{array}$$

whilst subsequent hydrolysis will yield the respective alcohols. In this way a possible mode of mechanism for the catalytic action of the sulphuric acid may be accounted for.

Further examples of the application of this principle may be cited. The addition of alkaline catalytic agents will tend to produce acidic substances, and *vice versa*. Such is the case in the Cannizzaro reaction,

$$2\mathrm{C_6H_5{\cdot}CHO} \xrightarrow{\mathrm{KOH}} \mathrm{C_6H_5{\cdot}COOH} + \mathrm{C_6H_5{\cdot}CH_2{\cdot}OH},$$

in the effect of acids on the organic nitro-compounds, in the keto-enol isomeric substances, and also in the conversion of unsaturated acids into $\alpha\beta$-derivatives in the presence of acids, *e.g.*,

$$\mathrm{CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH} \rightarrow \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}}\overset{(x)}{\mathrm{CH}}\mathrm{{\cdot}COOH},$$

the tendency in this case being to increase the reactivity or labile nature of the last hydrogen atom (x), which as we have noted in the case of atomic groupings of high reactivity may react with caustic soda or sodium ethoxide to form a

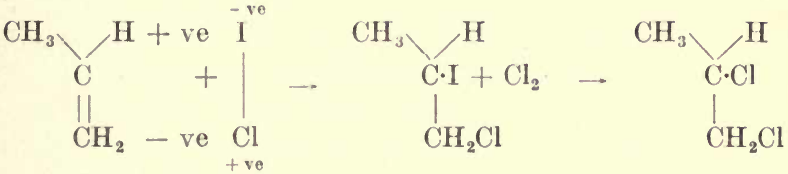
$$\mathrm{{:}CNa{\cdot}COOH}$$

derivative. In the cases of conversion of $\beta\gamma$- and some $\gamma\delta$-unsaturated acids into the $\alpha\beta$-derivatives, no secondary reaction of this nature does in fact take place, since the reactivity of the labile hydrogen is never sufficiently great. The caustic soda is thus a purely catalytic agent.

The same instance can be noted in the case of butyl acetylene, $(CH_3)_2C\cdot C\vdots CH$, which, when gently warmed, passes into dimethyl allylene, $(CH_3)_2C{:}C{:}CH_2$, whilst on treatment with metallic sodium the reverse change takes place.

The catalytic activity of a trace of iodine in the addition of chlorine to an unsaturated compound is readily intelligible from this point of view. It is at first sight difficult to see why I·Cl should be more reactive than Cl·Cl, since the formation of the iodochloride is itself an exothermic reaction.

The relative differences in the electro-positive and electro-negative nature of the couplet Cl·I, however, compensate for the loss of energy and permit of a relatively higher reactivity.



It would appear that the stability of any organic compound is dependent on its electronic character and its symmetry. Additive agents only exert a catalytic activity when there is a tendency to salt formation due to the above considerations; thus the problem resolves itself into a formulation of the intermediate compound theory in which the stability of the intermediate compounds is governed by electronic forces.

The inherent difficulty in the development of this theory to explain both organic chemical reactions in general and catalytic action in particular lies in the fact that we have no means of measurement of the electro-positive or negative nature of an atom or a grouping of atoms within a molecule; we can merely state that halogens and acid radicals are opposite in character to the hydrogen atom and hydrocarbon radicals, whilst increasing unsaturation increases the acid or electro-negative character of a hydrocarbon nucleus. The measurement must naturally include two factors, the absolute value and the effect of spatial arrangement on the electronic nature of neighbouring atoms.

CHAPTER XI

FERMENTS AND ENZYME ACTION

The development of the chemistry of the enzymes has followed that of organic chemistry through a sequence of changes curiously similar in point of view.

Prior to the time of Liebig, the dependence of various actions of fermentation on vital processes, such as the growth of yeast-cells, was generally accepted. Liebig and his school, although unable to accept the vitalistic theory of fermentation, could only submit a vibrational theory as a substitute, in which the decomposition of sugar and similar substances into simpler derivatives resulted from a shock given to the sugar molecules by the rapid decomposition of some substance in the living cell. In 1850, Pasteur conclusively proved that various fermentations were the result of certain intercellular chemical changes effected by the living organisms.

The chemical nature of fermentation processes was thus recognised, but a sharp distinction was still drawn between such processes and those brought about by organic catalysts prepared by extraction of certain living substances; such actions had long been known. Thus Récumier (1752) and the Abbé Spallanzani (1785) proved that gastric juices were able to dissolve pieces of meat outside the living organism. In 1830, Dubrunfaut[1] prepared an extract of malt which converted starch into sugar and in 1833 Payer and Persoz[2] isolated, from a watery extract of barley by fractional precipitation with alcohol, a substance, which they termed "diastase," possessing marked catalytic activity in the

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[1] *Bull. des Sciences, Technol.*, Paris, 1830.

[2] *Ann. Chim. Phys.*, 1833, **53**, 73.

conversion of starch into sugar. A year later, Schwann isolated from the gastric juice "pepsin," an enzyme bringing about hydrolysis of the proteins. The isolation of the enzyme "emulsin" from bitter almonds by Liebig and Wöhler in 1839[1] added another enzyme of historical interest to an ever-increasing number.

It was not, however, until 1896 when E. Buchner[2] showed that ruptured yeast-cells would yield under pressure a substance, "zymase," having all the fermentative properties of living yeast-cells, that the broad distinction between fermentative and enzyme reactions finally broke down and that all such processes could be attributed to the presence of certain chemical substances, termed enzymes, either secreted (intracellular) or excreted (extracellular) by living cells.

Enzymes are therefore to be regarded as catalysts produced by living organisms. Their synthesis in the laboratory has not as yet been accomplished.[3]

Although most of the enzyme actions actually studied involve the disintegration of complex molecules into simpler derivatives, yet experiments have shown that in the cases investigated synthetic changes are also brought about in the presence of the same enzyme. Croft Hill[4] was the first to point out the possibility of reversion or of synthesis as well as decomposition by using the same enzyme to arrive at equilibrium of reactants and products from both ends. His experiments were conducted with maltase, an enzyme catalytically active in the conversion of maltose into glucose by hydrolysis. By the action of maltase on glucose in aqueous solution, reversal to a maltose–glucose mixture was effected, equilibrium could be arrived at from both ends, but reversal with dilute solutions could not be obtained, possibly owing to the formation of another disaccharose revertose or isomaltose.[5]

Emmerling synthesised the glucoside amygdalin from a solution of glucose and mandelic nitrile in the presence of

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[1] *Annalen*, 1839, **22**, 1.

[2] *Ber.*, 1897, **30**, 117 *et seq.*

[3] Bayliss, "The Nature of Enzyme Action," London, 3rd edn., 1914.

[4] *J. Chem. Soc.*, 1898, **73**, 634.

[5] See Emmerling, *Ber.*, 1901, **34**, 600.

maltase, whilst equilibrium from both ends was obtained in a most convincing manner by Kastle and Lövenhart[1] by the action of lipase on ethyl butyrate and a mixture of ethyl alcohol and butyric acid. Hanriot,[2] in 1901, extended this work to the formation of glycerides from the lower fatty acids and inorganic acids, whilst in 1903, Pottevin[3] successfully synthesised glyceryl oleate by means of lipase. W. Bayliss[4] obtained equilibrium from both sides in the system glycerol glucose, glycerol, glucoside, and water with the aid of emulsin as catalytic agent.

It may further be noted that the second criterion of catalytic action, viz., that small quantities of the enzyme will effect practically unlimited conversion, has been tested from time to time by various observers. Thus Hammersten noted that rennet could clot more than 400,000 times its weight of caseinogen and O'Sullivan and Thompson[5] observed that invertase had not lost its activity after effecting the hydrolysis of more than 200,000 times its weight of saccharose.

Enzymes must therefore be regarded as catalytic agents, but we shall have occasion to note in the following pages many interesting peculiarities in the nature and mode of action of enzyme catalysts, which slightly differentiate enzyme action from ordinary catalytic processes. These differences, however, are not to be attributed to the interference of any vital process, since the investigation of Bredig and his co-workers have shown that similar anomalous results can be obtained with colloidal metals and certain metallic oxides,[6] and can be fully accounted for by the consideration of the physical and chemical nature of enzymes themselves, as well as by reactions which they effect, very different from the homogeneous and heterogeneous reactions described in the previous chapters of this book.

It may be stated that our present knowledge of enzyme action permits us to explain the somewhat frequent anomalies and points of difference from other catalytic processes more readily than to account for the striking analogies observed

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[1] *J. Amer. Chem.*, 1900, **24**, 491.

[2] *Compt. rend.*, 1901, **132**, 212.

[3] *Ibid.*, 1903, **136**, 769.

[4] *J. Physiol.*, 1913, **40**, 236.

[5] *J. Chem. Soc.*, 1891, **59**, 46.

[6] See p. 384.

and clearly demonstrated, not only by Berzelius,[1] but also by the more recent workers in this field.

THE NATURE OF ENZYMES

Although no enzyme has been isolated in a pure state, yet, from an examination of carefully purified preparations, it is practically certain that they are substances of high molecular weight. Physically they are colloidal in nature, and will only pass through dialysis membranes with extreme slowness. It is to this property, viz., their colloidal nature, that the differences between enzyme action and other catalytic processes are chiefly due.

Chemically they are relatively unstable, being easily destroyed by boiling water. Their constitution is at present unknown; although many give the protein reactions, yet, in certain oxydases, the quantity of nitrogen is so small as to lead one to suspect its presence as an impurity. More important is the fact that enzymes always leave an ash on ignition; small quantities of certain elements, notably iron, manganese, magnesium, and calcium, and, in certain enzymes, chlorine and phosphorus, can always be isolated from the purest specimens.

Bertrand[2] laid great stress on the importance of the inorganic constituent of the enzyme, and has expressed the view that enzymes consist essentially of an albuminous organic colloid associated with an inorganic colloid, which latter is the active catalyst, the "co-enzyme" or "co-ferment." He regards the following elements as being the basis of enzyme catalytic activity: manganese in the oxydases and calcium in coagulation processes, whilst iron is associated with hæmoglobin, magnesium with chlorophyll, and iodine in the thyroid gland.

Bertrand[3] cites in support of his theory, the interesting oxydase isolated by Yoshida,[4] "laccase," the natural catalyst in the autoxidation process[5] of the sap of the lac tree. Lac-

[1] *Lehrbuch*, 1848, **6**, 22.

[2] *Compt. rend.*, 1896, **122**, 1132.

[3] *Ibid.*, 1897, **124**, 1032.

[4] *J. Chem. Soc.*, 1883, **43**, 472.

[5] See p. 143.

case contains small quantities of manganese (up to 2 per cent. in the ash) and addition of manganese salts greatly increases the activity of the enzyme.

Dony-Hénault[1] has actually prepared an artificial "laccase" by repeated precipitation by means of alcohol of a protected colloidal manganese hydroxide from an aqueous solution containing 2 per cent. of manganese formate, 0·8 per cent. of sodium bicarbonate, and 20 per cent. of gum arabic as protective colloid.

The specific nature of enzyme action.—This simple theory, put forward by Bertrand, does not, however, account for that most mysterious property of enzyme action, viz., the specific action of each enzyme.

We may roughly divide the reactions catalytically accelerated by enzymes into three groups.

I. Coagulating enzymes: including those enzymes which catalytically accelerate the coagulation of many natural fluids, such as blood, muscular plasma, and caseinogen in milk. We shall, however, have occasion to note that the process of coagulation is in reality a colloidal manifestation, and is usually brought about by suitable alteration of the nature of the suspension medium. For this reason, many investigators consider that coagulating enzymes should not be characterised by this property of coagulation, and therefore form no distinct class.

II. Enzymes inducing hydrolysis, which in turn may be sub-divided into the following reactions:

Saccharoclastic reactions.
Hydrolysis of the glucosides and glycerides (lipoclastic).
Protein hydrolysis (proteoclastic enzymes).

III. Enzymes inducing oxidation or reduction: the oxydases and the reductases.

Bertrand's hypothesis would appear tenable if the various enzymes acting catalytically in the above processes could also be divisible into three groups, and if in each group one enzyme were replaceable by another of the same group. We have already noted that with inorganic catalysts rough groupings may be compiled, such as certain oxides for processes

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[1] *Bull. Acad. Roy. de Belgique*, 1908, 105.

of oxidation, reduced metals for hydrogenation, and irreducible oxides for dehydration and dehydrogenation, and we might postulate an even more rigid classification for the enzymes in each group. But, in actual fact, enzymes are not interchangeable to the extent which would be logically expected from Bertrand's hypothesis. Although the extreme view frequently stated, that each individual chemical reaction requires its own particular enzyme which is inoperative for any other reaction, is not entirely correct, yet the specific nature of enzyme action is so marked as to demand an inquiry into the reason.

VARIETIES OF ENZYME ACTION

I. **Coagulating enzymes.**—Thrombase, is the active catalyst in the clotting of certain albuminoids in the blood termed, collectively, fibrinogen. Fibrinogen on coagulation is converted into a stringy substance, fibrin, white in colour when freed from the blood pigment which it absorbs. Thrombase makes its appearance in the white corpuscles in the blood, whilst smaller quantities are formed in the red. We have already referred to the importance of calcium salts in coagulating processes and in the case of blood clotting the calcium ions perform two important functions, first, they are indispensable for the formation of thrombase from pro-thrombase, which apparently results from the interaction or coupling of an enzyme serozyme and a lipoid thrombokinase[1]; secondly, they appear necessary for the interaction of thrombase and the fibrinogen. Calcium ions may therefore be regarded as a co-enzyme to thrombase. The activity of thrombase is unimpaired in the clotting process, but it is gradually absorbed by the coagulated fibrin, and an apparent decrease in activity is consequently observed.

Similar to thrombase is the enzyme myosinase, which affects the clotting of myosinogen, the albuminous substances in the muscle serum.

Rennet, the active catalyst in the coagulation of caseinogen in milk causing a clot which carries down with it the milk

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[1] Nolf, *Arch. Inst. Physiol.*, 1908, **4**, 165; 1909, **7**, 280.

fat and the phosphates, is found in the gastric glands, various plants, *e.g.*, the papaia, and some micro-organisms. Rennet exists in the mucous membrane of the stomach in the form of pro-rennet, which is converted by dilute acid into the catalyst. The catalyst attains its maximum activity at 40°, and is more active in the presence of hydrogen ions than of hydroxyl ions. Calcium ions appear necessary for the coagulating process. It may be noted in passing that milk may be coagulated by calcium, barium, or strontium salts in the absence of rennet.

Pectase, in a similar manner, causes the clotting of several carbohydrates in plants.

II. **Enzymes inducing hydrolysis.**—(*a*) *Saccharoclastic reactions.*—The conversion of starch into glucose by enzyme action is one of the most important in the animal metabolism. Amylase, (diastase) is widely distributed both in the animal and vegetable world and can rapidly effect the "liquefaction" of starch. The products of this, the primary hydrolysis, are dextrins (amylodextrin, erythrodextrin, etc.), characterised by their reaction with iodine to give red absorption compounds distinct from the vivid blue obtained with the starches; the hydrolysis corresponds exactly with that obtained in the first stage of the hydrolysis of starch, using acids as catalysts.

It has been thought by some investigators, notably Fraenkel and Hamburg[1] that amylase was capable of resolution into two active enzymes; more recent investigation, however, has confirmed the individuality of the enzyme.[2]

The second stage of the hydrolysis of starch, the conversion of the dextrins into maltose, is accelerated by the enzyme dextrinase isolated by Duclaux,[3] whilst the final conversion of maltose into glucose is effected by maltase.

Similar to diastase in their power of accelerating the hydrolysis of complex polysaccharoses, and probably also capable of resolution into two or more individual enzymes, each of which effects part of the hydrolysis, are the following: cytase

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[1] *Beitr. Chem. Phys. u. Path.*, 1906, **8**, 3, 89.

[2] Wohl and Glimm, *Biochem. Zeitsch.*, 1910, **27**, 349; see also Lintner and Düll, *Ber.*, 1893, **26**, 2533; Brown and Morris, *J. Chem. Soc.*, 1889, **55**, 462.

[3] *Traité de Microbiologie*, 1899, p. 71.

or cellulase, effecting the hydrolysis of cellulose into reducing sugars, inulase hydrolysing inulin to fructose, and pectinase and gelase degrading pectins and agar-agar to reducing sugars. It is interesting to note that inulase is without action on starch.

Several important enzymes effect the hydrolysis of the simpler saccharoses. Thus, reference has already been made to the enzyme maltase, accelerator to the hydrolysis of maltose into glucose.

Invertase and lactase effect similar hydrolytic decompositions of cane-sugar and lactose respectively, the former being converted into fructose and glucose and the latter into galactose and glucose. For many other disaccharoses, similar hydrolytic enzymes have been isolated.

(*b*) *The glucosidoclastic enzymes.*—It is somewhat remarkable that the complete elucidation of the structure and configuration of the carbohydrates, with the possible exception of the complex starches, was accomplished with the aid of very few chemical reactions.

Sugars are aldehydic or ketonic alcohols and the isolation and synthesis of fourteen out of the possible sixteen hexoses, seven out of the eight pentoses, the tetroses, the trioses and glycollic aldehyde, $CH_2OH{\cdot}CHO$, the first sugar, has been due chiefly to the systematic work of Emil Fischer, who utilised the osazone reaction for the isolation and purification of the sugars. The reactions involved in the synthesis or degradation of the sugars are usually those affecting the aldehydic or ketonic grouping, such as the addition of HCN to form cyanhydrins skilfully employed by Kiliani in synthetic operations, and Wohl's hydroxylamine reaction, or Ruff's interesting application of Fenton's method of oxidation by means of hydrogen peroxide, using an iron salt as catalyst[1] in the degradation.

The selective nature of enzyme action is most marked in the saccharoclastic and glucoside splitting processes. As has already been observed, the action depends, not only on the nature of the enzyme, but also on the molecular configuration as well as the sense of rotation of the sugar.

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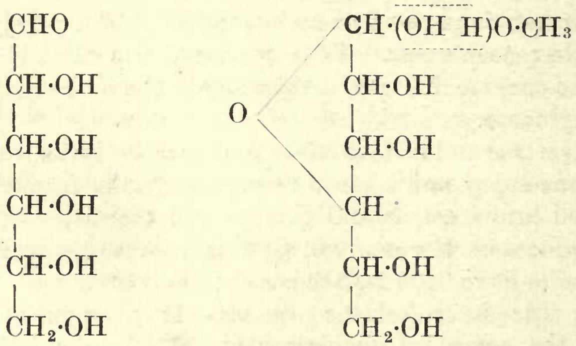
[1] See p. 142.

Since the glucosides neither reduce Fehling's solution nor react with phenylhydrazine, we must therefore assume that they do not possess an aldehyde or ketonic grouping. Thus :

d-Glucose must react as a closed anhydride [1]



Fischer and v. Ekenstein, in fact, isolated from the etherification of glucose by means of methyl alcohol in the presence of hydrochloric acid the two methyl glucosides *a* and *β*.[2]

The introduction of a new asymmetric carbon atom **C**, should thus result in the formation of two isomers.[3]

These two methyl glucosides readily undergo hydrolysis with dilute acids and with certain enzymes. Thus, the *a*-derivative is affected by maltase, whilst the *β*-derivative, although not hydrolysed by maltase, is easily affected by emulsin, the enzyme secreted in bitter almonds. Emulsin is one of the most important glucosidoclastic enzymes, inducing the hydrolysis of a great variety of natural glucosides, such as amygdalin, salicin, arbutin, phloridzin, and æsculin. This important experiment on the *a*- and *β*-methyl glucosides leads one to assume that amygdalin is a *β*-glucoside, whilst maltase must be regarded as an *a*-glucoside, *i.e.*, an *a*-*d*-glucose-glucoside. We may therefore assume with Bayliss that revertose (isomaltase) isolated by Croft Hill in studying the glucose–water–maltose equilibrium is nothing more than *β*-*d*-glucose-glucoside. A few other glucoside hydrolytic enzymes have been isolated, such as lotase and rhamnase,

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[1] See page 338.

[2] *Zeitsch. physikal. Chem.*, 1898, **26**, 61.

[3] See *ante*, p. 337.

but have not been closely investigated. Mention may be made of three which have some technical importance, viz., erythrozyme, effecting the hydrolysis of rubrerythric acid in the madder plant to alizarin and glucose, and indimulsin, catalytically hastening the hydrolysis of the indican in the indigo plant to indoxyl and indiglucin, and, lastly, tannase, a glucosidoclastic enzyme degrading tannins to glucose and the various acids, such as gallic and ellagic acids.

(*c*) *Lipoclastic enzymes.*—Lipase, isolated from the pancreatic juice of animals and many seeds during the period of germination, has a very wide distribution, and is one of physiological importance. It is catalytically active in processes of esterification and hydrolysis of esters, and its activity is not limited to the glycerides of the higher fatty acids. We have already noted that its function is definitely catalytic in both hydrolysis and esterification.

It is worthy of note that lipase itself exhibits some selective properties, since *d*- and *l*-fats do not undergo hydrolysis at the same rates, and in the case of ethyl mandelate the *l*-ester alone is saponified.[1]

We shall, however, defer the consideration of the reaction kinetics of the process to a future section.

It may be noted that Magnus[2] claimed to have isolated a dialysable co-enzyme for lipase by continued dialysis of extract of liver. It was afterwards shown that the co-enzyme was in reality bile-salt, which increased the dispersion and therefore the surface area of the colloidal enzyme.

(*d*) *The proteoclastic enzymes.*—These include some of great physiological importance, since the *rôle* of nitrogen in both animal and vegetable physiology is an all-important one. The final synthesis of complex proteins from free atmospheric nitrogen and the subsequent degradation of the complexes into simpler derivatives can be accomplished entirely by a series of enzyme reactions unparalleled in variety and number in any other branch of the subject.

We may classify the reactions taking place in the various stages of the nitrogen cycle according to the following diagrammatic representation.

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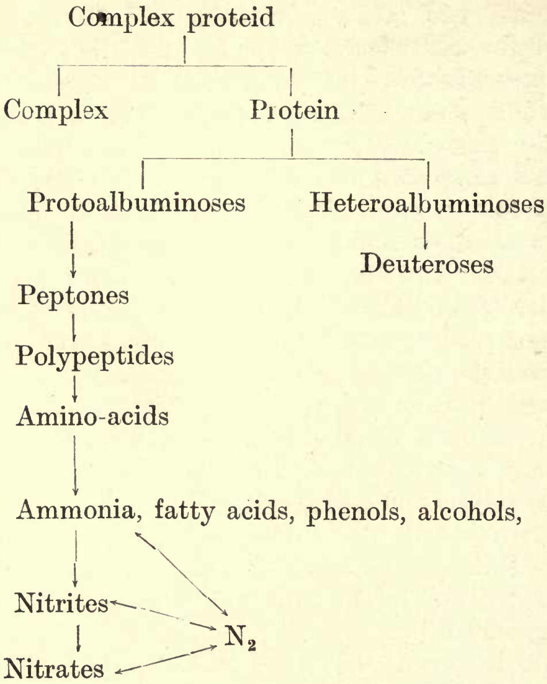
[1] Dakin, *Proc. Chem. Soc.*, 1903, **19**, 161.

[2] *Zeitsch. physikal. Chem.*, 1906, **48**, 376.



The complex proteins have been but little investigated on account of the great difficulty of isolating a pure material.

Mention may be made of the chromoproteins, which usually consist of a colourless protein united with a coloured complex group (the prosthetic group).

For example, hæmocyanine and hæmoglobin are similar chromoproteins, in the former of which copper replaces the iron present in hæmoglobin.

Oxyhæmoglobin is easily hydrolysed into its simpler derivatives hæmatin and the protein globin.

The nucleoproteins isolated from animal tissues and the spermatozoa of fish undergo simple hydrolysis with the enzyme pepsin to nucleins and a protein. The nuclein itself, however, still contains a hydrolysable protein constituent and a nucleic acid, which hydrolysis can be effected with the enzyme trypsin or with dilute acids. The nucleic acids, when subjected to acid hydrolysis, yield a variety of products, such as purin bases, pentoses, and phosphoric acids. Somewhat similar to the nucleoproteins are the phosphoproteins, in which the nucleic acids formed on hydrolysis of the complex are usually much simpler in composition than those derived from the nucleoproteins. Amongst the more important may be mentioned casein from milk, ichthulin from fish eggs, and vitellin from hen egg yolks.

Certain glucoproteins, such as the mucoids and mucins, contain both a protein and a carbohydrate grouping easily isolated by hydrolysis. From chitin, the interesting simple aminocarbohydrate glucosamine can be isolated.

Many unclassified proteins are of extreme importance both physiologically and in technical processes; thus, keratin, the main constituent of hair and horn, gelatin in bone and cartilage, and fibrosin in crude silk.

The proteins themselves naturally vary in composition according to their origin, and have also been subjected to a somewhat loose classification on this basis. Amongst the more important groups may be mentioned the histones and protamines, including the proteins isolated from hydrolysis of the chromo- and phospho-nucleoproteins and the albumoses and globulins, the water soluble and insoluble proteins of animal and vegetable tissues.

The proteoclastic enzymes are most conveniently classified according to their hydrolytic power on albumen, and we may distinguish the following more important groupings: pepsin, the trypsins, erepsins, and amidases.

Pepsin is the most important enzyme causing gastric digestion. The enzyme itself can be isolated from the glands of the mucous membrane and of the stomach in the form of a white powder soluble in acidulated water and 5 per cent. alcohol. It is not dialysable and can be precipitated by salts or absolute alcohol, and is thus albuminoid in character itself. In fact, when subjected to acid hydrolysis, tyrosine, leucine, alanine, and other amino-acids result.

Its proteoclastic activity is enhanced in the presence of hydrogen ions, the optimum corresponding with a 0·2 per cent. HCl solution. The quantity of acid to be added, however, varies with the amount of pepsin present, owing to the absorption of hydrogen ions by the enzyme (see p. 376).

It is probably not secreted as an active enzyme, but as a pro-enzyme, pepsinogen, which is converted into pepsin by dilute acids.

The products of hydrolysis of proteins brought about by means of pepsin are chiefly proteoses and peptones, and it is only on prolonged digestion that further hydrolysis to the simpler amino-acids occurs. It is interesting to note that, although direct synthesis of a known protein from peptones has not been accomplished by means of pepsin, yet the reversibility of the proteoclastic processes catalytically accelerated by pepsin has been indicated in the formation of plasteins from peptones by Danilewski.[1] The synthesis of the so-called paranucleins by B. Robertson[2] was shown by W. Bayliss[3] to be fictitious, since the observed precipitates were found to result from colloidal precipitation of substances in the pepsin employed.

Trypsin is the most important proteoclastic enzyme of the pancreas. Its action on albuminoids is similar to that of pepsin, but hydrolysis proceeds further, polypeptides and amino-acids being the chief products of hydrolysis. The optimum activity is observed in a feebly alkaline solution.

The pro-enzyme zymogen or trypsinogen is converted into the active enzyme trypsin, not only by calcium ions as shown by Delezenne[4] and Ayrton,[5] but also by another catalyst, enterokinase.[6]

Enterokinase must therefore be regarded as a catalyst for a catalyst, and is the only case at present recorded.

Trypsins are widely distributed, both in animals, vegetables, and moulds. Thus in yeasts, endotryptase has been isolated, an intracellular enzyme practically identical with trypsin in proteoclastic activity.

Erypsin.—These proteoclastic enzymes cannot effect the hydrolysis of the natural proteids, but act on the products of hydrolysis produced by pepsin and trypsin, viz., the albu-

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[1] "The Organoplastic Forces of the Organism," Kharkoff, 1886.

[2] *J. Biol. Chem.*, 1907, **3**, 95.

[3] *J. Physiol.*, 1913, **46**, 236; 1907, **5**, 493.

[4] *Compt. rend. Soc. de Biol.*, 1905, **57**, 476.

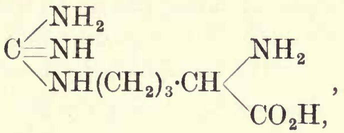
[5] *Quart. J. Exp. Physiol.*, 1909, **2**, 201.

[6] Bayliss and Starling, *J. Physiol.*, 1905, **32**, 129.

moses and peptones. Some, such as erypsin, will even hydrolyse pepsin itself, whilst others can only effect hydrolysis of relatively simple polypeptides into the simpler amino-acids.

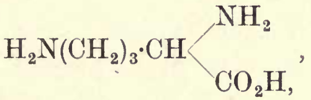
(*e*) *The amidases.*—These include a number of enzymes, but little investigated, which can effect the hydrolysis of the simpler amino-acids themselves into ammonia or urea and the fatty acids, phenols, or alcohols.

Thus arginase, an enzyme present in the liver, hydrolyses arginine:



$$\mathrm{C}\begin{matrix}\diagup\mathrm{NH_2}\\ =\mathrm{NH}\\ \diagdown\mathrm{NH(CH_2)_3{\cdot}CH}\begin{matrix}\diagup\mathrm{NH_2}\\ \diagdown\mathrm{CO_2H}\end{matrix}\end{matrix},$$

into urea and ornithine:



$$\mathrm{H_2N(CH_2)_3{\cdot}CH}\begin{matrix}\diagup\mathrm{NH_2}\\ \diagdown\mathrm{CO_2H}\end{matrix},$$

and can similarly convert guanidine into urea and ammonia.

The last four stages of the nitrogen cycle, resulting from the activity of the oxidation bacteria (nitromonas) which perform the conversion of ammonia to nitrites and nitrates, the denitrifying bacteria such as *Bacillus coli*, and *B. denitrificans*, α and β, and the nitrogen fixation bacteria, both Beyerinck's *Clostridum pastorianum*, and various fungi such as *Penicillium glaucum* and *Aspergillus niger*, as well as the symbiotic bacteria *Azotobacter* and Beyerinck's *B. radicicola*, which exhibits the phenomenon of alternate parasitism with leguminous plants, are of great technical significance in our agricultural industries, but an adequate discussion of the various applications of bacterial methods to the preparation of nitrogenous fertilisers lies somewhat outside the province of this book.

III. **The reductases and oxidases.**—The reductases have been but little investigated and no specific enzyme has yet been isolated. The reduction of nitrates to nitrites, of nitrites to ammonia, of sulphur to hydrogen sulphide and the preparation of colourless leuco-bases from such dyes as methyleneblue, can all be accomplished by bacterial means, but it still remains to be proved whether the reduction is not a normal reaction, unassisted by any catalytic activity. The oxydases, on the other hand, are more clearly defined, in that specific enzymes have been isolated which materially hasten the process of atmospheric oxidation; we have already referred to the interesting case of the manganese containing oxydase, laccase; œnoxydase is a similar ferment containing iron, causing "casse" in wines, destroying both their colour and taste.

In the complex case of chlorophyll, the mechanism of the catalytic enzyme activity is somewhat different. According to Usher and Priestley,[1] the chlorophyll serves merely as a light sensitiser to bring about the reaction:

$$3H_2O + CO_2 + \frac{\text{Light}}{\text{energy}} = H{\cdot}CHO + 2H_2O_2.$$

The protoplasm of the chloroplast serves to polymerise the formaldehyde to formose or methylentan, $C_6H_{12}O_6$, the simple sugar isolated by Butlerow in 1865, and subsequently reinvestigated by Tollens and E. Fischer, who showed that it was identical with *d-l*-fructose.

The hydrogen peroxide, which can always be detected in plant growth, is removed by a catalase present in the green leaves. We have already noted in the discussion on processes of autoxidation that, according to some investigators, in the presence of moisture, hydrogen peroxide is invariably formed during the process. This idea has been extended to enzymes by Bach and Chodat,[2] who postulated two forms of oxidising enzymes, both functioning as catalysts in the decomposition of hydrogen peroxide thus formed.

(i) The catalases, which eliminate molecular oxygen, and thus remove a toxic constituent from the system, and

(ii) The peroxydases, which eliminate active oxygen and thus actually assist in the process of oxidation. Certain oxydases have been isolated from the liver which catalytically hasten the oxidation of the purin bases to simpler products; thus, with the aid of the oxydases, guanase, xanthinoxydase

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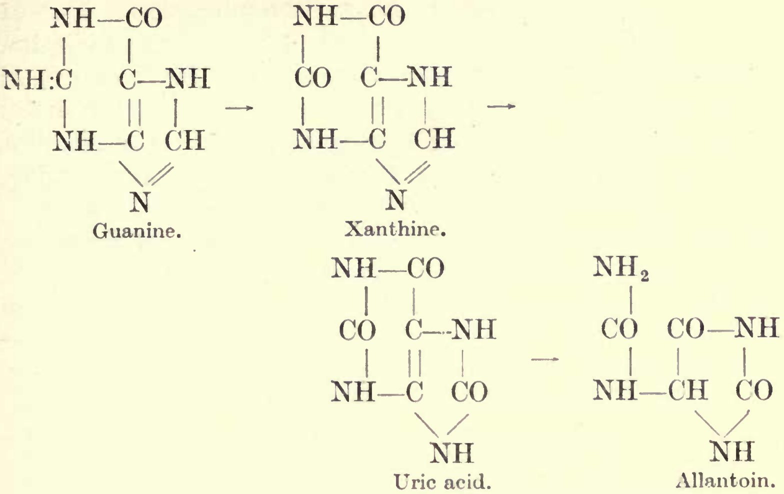
[1] *Proc. Phys. Soc.*, 1906, **78**, 3, 38.

[2] *Arch. d. Sci. Phys. et Nat. Geneva*, 1904, **17**, 4771.

and uricolase, guanine can be oxidised by atmospheric oxygen to allantoin, according to the following scheme :



The physiological use of uricolase for gout disorders thus suggests itself.

A number of interesting phenomena have been observed in studying the properties of the oxydase isolated from certain insects which exhibit luminosity at night, notably by Dubois,[1] by W. Coblentz on the Lampyrides,[2] and by McDermott, Very, and Langley on the American Fireflies.[3]

The biological production of light, according to these investigators, is the result of a chemical process of oxidation.

Dubois has ascribed the name luciferine to the substance undergoing oxidation. Luciferine is an albuminous substance precipitated by neutral salts and bases, but not by dilute acids. When undergoing oxidation in the cold, either by means of dilute solutions of oxidising substances such as permanganate of potassium or by an organic oxydase, it becomes luminous, the radiation being selective and practically cold. The natural oxidising agent is luciferase, a zymase containing iron associated with a complex protein. Both luciferine

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[1] *Thèses de la Faculté des Sciences de Paris,* 1886; Smithsonian Report, 413 (1895); Prometheus, Berlin, 291 (1895); *Compt. rend.*, 1911, **153**, 690; 1913, **155**, 730; and 1914.

[2] "A Physical Study of the Fire-Fly," Washington, 1912.

[3] *Bull. Bur. of Standards*, 1910, **6**, 3.

and luciferase appear to be secreted by the light-emitting insects and the light produced by them is at least partly due to the result of the interaction of these two substances. Dubois further maintains that the selective nature of the radiation emitted, conspicuous for the almost complete absence of any thermal effect, is not entirely due to the characteristics of the light emitted during the oxidation of luciferine, but is due to the presence of a third substance, luciferesceine, which is characterised by its fluorescent properties.

It would appear that luciferesceine performs at least two important functions, first, the transformation of heat radiation into light by fluorescence, and, secondly, the elimination of ultra-violet light, which might seriously affect the life of the insect which contains these interesting substances.[1]

ALCOHOLIC FERMENTATION

The oxydases most important technically are those associated with processes of fermentation. The earliest fermentation process was that associated with the preparation of alcoholic liquors from sugars and starches.

We have already referred to the hydrolysis of starch into sugars by the aid of the enzyme diastase and, in the manufacture of beer, the sugary liquid so produced, termed "wort," is then subjected to alcoholic fermentation after the addition of hops, filtration, and sterilisation by boiling.

The conversion of the glucose into ethyl alcohol and carbon dioxide, which is brought about by various yeasts (*Saccharomyces*), from which Buchner isolated the specific enzyme zymase, thus reconciling the fermentation and enzyme theories of these catalytic reactions, is not strictly a process of oxidation :

$$C_6H_{12}O_6 \rightarrow 2C_2H_5{\cdot}OH + 2CO_2,$$

but since both dioxyacetone[2] and lactic acid[3] have been

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[1] For more recent studies of Bioluminescence, see Harvey, *Amer. J. Physiol.*, 1916, **41**, 454; 1917, **42**, 318; *J. Gen. Physiol.*, 1918, **1**, 133; 1919, **1**, 269; *J. Biol. Chem.*, 1917, **31**, 311.

[2] Buchner and Meisenheiner, *Ber.*, 1910, **33**, 1773; Kroop and Windaus, *Beitr. z. Chem. und Phys. u. Path.*, 1905, **6**, 392.

[3] Nef, *Annalen*, 1904, **335**, 191.

isolated from the fermenting liquid, it has been postulated that these bodies are formed as intermediaries in the process and that zymase must therefore consist of a complex number of enzymes containing both oxydases and reductases.

Various yeasts classified as top and bottom yeasts are used in the brewing industries to effect this fermentation process, and by such a fermentation proof spirit of from 4 to 24 per cent. can be obtained.

A similar combined amyloclastic and fermentative process is applied to the production of both malt and grain whiskey. Attempts to utilise organisms which contain both enzymes, amyloclastic and fermentative, thus producing alcohol in one operation instead of two, have met with some measure of success in the amylo-process, which, with the discovery of new and more vigorous organisms containing both enzymes, has now become a technical operation.

Various troubles met with in the production of both beer and whiskey are associated with the presence of enzymes produced by adventitious organisms, such as ropiness in beer due to *Bacillus viscosus*, sarcina turbidity, sediment due to the *Saccharobacillus pastorianus*, bitterness due to the wild yeast, especially *Saccharomyces pastorianus*, and acidity due to the production of acetic acid.

In the production of wine from the expressed juice of the grape "must" which contains from 15 to 33 per cent. of glucose, fermentation is usually produced by *Saccharomyces ellipsoideus* I, giving a 10 per cent. alcohol content in champagne and up to 16·2 per cent. in port.

Wine is especially sensitive to spoiling by adventitious ferments. We have already mentioned the causes of "casse," whilst souring, due to the formation of acetic acid by *B. aceti*, *B. pastorianum*, or *B. Kuntsingianum* or of lactic acid by *B. acidi lactici*, is especially frequent. Ropiness and turbidity caused by *B. viscosus* and certain micrococci are more rarely met with.

In the production of ginger beer, the symbiotic bacteria *Saccharomyces pyriformis* and *Bacterium vermiform* are used as a source of fermenting enzymes.

ACID FERMENTATIONS

Acetic acid.—The oxidation of ethyl alcohol to acetic acid is largely accomplished, especially where the production of crude dilute acetic acid or vinegar is contemplated, by means of a biochemical oxydase. The oxydases capable of catalytically accelerating this process of atmospheric oxidation are found in several organisms, more especially in *B. aceti*, *B. pastorianum*, *B. xylinum*, and *B. Kuntsingianum*, whilst actual isolation of the active enzyme has been accomplished by Buchner and Meisenheiner.[1]

Wine is frequently used as raw material and aeration and oxidation is brought about in casks. During recent years, the quick vinegar process has been introduced, in which small beechwood shaving contact towers are used to support the bacteria and to serve as oxidation towers for the alcohol.

Lactic and butyric acids.—The production of lactic acid from glucose, rhamnose, galactose, mannitol, sorbitol, and inositol can be accomplished by a variety of oxidising enzymes, especially that present in Pasteur's *B. acidi lactici*,[2] whilst the formation of butyric acid from the lactic acid so formed often proceeds simultaneously, due to the presence of certain reductases in organisms present with the oxidising bacteria, *e.g.*, *B. butyricus*:

$$CH_3{\cdot}CH{\cdot}OH{\cdot}COOH \rightarrow CH_3{\cdot}CH_2{\cdot}COOH.$$

Technical applications of these fermentative reactions are to be found in the preparation of sour milk, koumiss, kephir, and of butter in which slight souring is desirable to enable the churning operation to proceed more smoothly, to aid preservation, to improve the flavour, and to increase the yield. An artificial aroma is frequently introduced into butter by the addition of special strains of bacteria to the cream, whilst defects such as fishy, bitter, or turnip flavours in butter are usually due to adventitious organisms, such as *B. foetidus lactis*, *B. fluorescens liquefaciens*, or *Oidium lactis*.

Cheese-making is also a biochemical industry in which the

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[1] *Ber.*, 1903, **36**, 634.

[2] See Herzog, *Zeitsch. physiol. Chem.*, 1903, **37**, 381.

caseinogen separated from the milk by rennet is allowed to ripen for several weeks under the influence of certain enzymes. Lactic acid, and caseinoclastic and gas-producing enzymes are usually necessary, and the extraneous bacteria are frequently present. In Cheddar cheese, *B. acidi lactici* alone is necessary, whilst in Roquefort and Gorgonzola the green mould, *Penicillium glaucum*, is largely employed.

Bitter and coloured cheeses are frequently caused by extraneous bacterial growth producing objectionable products by oxidation or hydrolysis, especially tyrothrix, *Geniciolatus* and *Micrococcus casei*.

Other industrial uses of oxydases and reductases present in organisms are to be found in various retting processes, *e.g.*, flax, hemp, sisal, etc., and in the puering of hides by pickling after liming, lactic acid being produced chiefly by *Bacillus furfuris* as well as in tanning itself, where lactic acid is produced by the activity of *B. corticalis*. In the curing and sweating of tobacco leaves, enzyme activity performs a most important function. Partial hydrolysis of the starches, protein matter, fats, and tannin takes place during the curing process, whilst, in the fermentation stage itself, part of the nicotine and tannin is oxidised and the aroma is developed. The organisms *B. mycoides*, *B. subtilis*, and *B. tobacci* supply some of the more important enzymes for this stage of the process.

Fermentation is usually accomplished at 52° in a humid atmosphere, and it is rather the influence of humidity which appears to govern the production of a good aroma than the presence of adventitious organisms.

The importance of enzyme activity in the disposal of sewage, in the treatment of industrial trade wastes, and in the purification of water during the processes of slow sand filtration and storage are well known, but for the discussion of such complex changes, reference may be made to standard works on these subjects.

An important development of enzyme activity must be briefly noted, namely, the conversion of starches into acetone, carbon dioxide, hydrogen, and a small quantity of methane.

In the conversion of starches into ethyl alcohol by fermentation processes, the presence of small quantities of acetone and fusel oil as products of various complicated side reactions, objectionable in wines and spirits, can scarcely be avoided, even under the optimum conditions for the production of ethyl alcohol. Several investigators, however, have shown the possibility of the technical production of both acetone and fusel oil from starches with a corresponding diminution in the yield of ethyl alcohol. Both acetone and fusel oil are required in ever-increasing quantities by the chemical industries, the former as a solvent for various purposes such as certain aeroplane dopes and explosives and the manufacture of chloroform, the latter when mixed with a nitrocellulose base for varnishes, whilst from both substances the possibility of an economic synthesis of rubber has been demonstrated by various workers, such as Harries, Perkin, Hoffmann and Coutelle, Matthews and Strange, and others.

The idea was first developed on an industrial scale by Fernbach,[1] who showed that, under suitable conditions, starches from various sources, such as maize or rice, potato, or even chestnut and acorns, could be fermented into a mixture of acetone and fusel oil in the ratio of approximately 1 : 2.

The composition of fusel oil varies with the nature of the starch employed and with the organism which accelerates the process of fermentation ; it consists essentially of a mixture of the higher aliphatic alcohols, especially isoamyl alcohol. Budakoff[2] gives the following analysis of a potato fusel oil.

	Per cent.
Isopropyl alcohol	8·7
Isobutyl alcohol	9·8
Amyl alcohol	87·9

Mycoderma ellipsoideus yields chiefly *n*-amyl alcohol, whilst the beer organism *M. cerevisiae* chiefly isobutyl and isoamyl alcohols.

Morin, in 1888,[3] first showed that a 10 per cent. yield of *n*-amyl alcohol was obtained when glycerine was subjected to fermentation by means of a certain bacillus isolated by Fitz, the so-called Fitz's *B. butylicus*.

At a later period, Emmerling[4] showed that with pure cultures but small yields of fusel oil were obtained, and that

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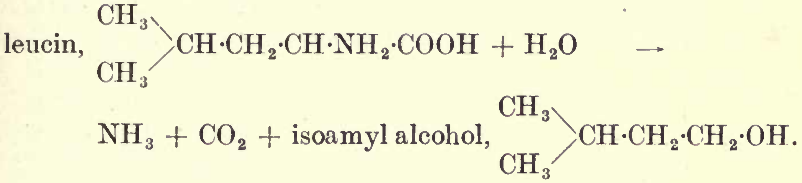
[1] F.P. 448364/1913.

[2] *Chem. Zeit.*, 1903, **28**, 187.

[3] *Compt. rend.*, 1888, **105**, 819.

[4] *Ber.*, 1904, **37**, 353.

various organisms, notably *Granilobacter butylicum*, *B. orthobutyricus*, and *B. mesentericus vulgaris*, were active in the production of the higher alcohols, notably butyl alcohol. Ehrlich's[1] experiments revealed the fact that the production of fusel oil was governed by a remarkable cycle of reactions. He showed that the higher alcohols resulted from the hydrolysis of the simple amino-acids thus :



$$\text{leucin, } \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot CH\cdot NH_2\cdot COOH + H_2O \rightarrow$$

$$NH_3 + CO_2 + \text{isoamyl alcohol, } \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot CH_2\cdot OH.$$

Isoleucin, in a similar manner, yields active amyl alcohol, whilst aminovaleric and glutaminic acids yield isobutyl and *n*-propyl alcohols respectively.

The ammonia thus liberated is subsequently reabsorbed by the yeast-cells to form a protein of high complexity, which then undergoes secondary hydrolysis to the simpler amino-acids, and the process starts *de novo*.

Although Ehrlich was not successful in isolating an enzyme capable of effecting the hydrolysis of the amino-acids, yet Effront showed that amylase, an enzyme isolated from an ordinary fermentation process, was capable of hydrolysing amino-acids completely in seventy hours. To ensure the production of fusel oil in quantity, the presence of protein material is therefore desirable, and various devices have been adopted to ensure its presence. Dubosc[2] suggests the uncrystallisable residues of beet-sugar refineries, Ehrlich[3] hydrolysed albumen, Mislin and Lewin[4] seeds of leguminous plants, and, lastly, Fernbach[5] utilises a small quantity of sterilised yeast degraded by the action of a ferment such as *Tyrothrix tenuis*, or by means of steam. Fernbach's process can be briefly outlined as follows :

Maize or other carbohydrate (including the pentosans obtained by the acid hydrolysis of wood) is sterilised at 130°,

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[1] D.R.P. 177174/1905.

[2] "Rubber, Its Production, Chemistry and Synthesis," Griffin, 1918, p. 300.

[3] E.P. 6640/1906.

[4] E.P. 10435/1903.

[5] *Loc. cit.*

made into a wort with water, and a small quantity of degraded yeast is added; the mixture is then again sterilised by heat. After cooling, an anaerobic fermentation process is conducted by means of a bacillus such as Fitz's *B. butylicus* at a temperature of 30° to 35°. The mass is then distilled, and a yield of from 33 to 50 per cent. of acetone and fusel oil on the carbohydrate employed is usually obtained.

No adequate explanation for the production of acetone during the process of anaerobic fermentation is as yet forthcoming.

THE RESOLUTION OF OPTICALLY ACTIVE SUBSTANCES BY MEANS OF ENZYMES

In 1860, Pasteur observed the selective action of the enzyme of a mould, *Penicillium glaucum*, on the oxidation of racemic ammonium tartrate, and noted that the *d*-form was practically entirely destroyed, leaving the *l*-form untouched.

Schizomycetes (including *Aspergillus mucor* and *A. niger*, *B. ethaceticus* and *B. termo*), on the other hand, assimilate the *l*-form, leaving *d*-ammonium tartrate unchanged.

Pasteur's original investigations have been greatly extended and amplified, but owing to the complete loss of one enantiomorph and the small yield of the other, this method of resolution is usually only applied for diagnostic purposes, where optically active racemates are expected to be present.

More recent work has shown that enzymes present in various micro-organisms may have the following actions on enantiomorphs:

(1) They may assimilate or destroy only one form.
(2) They may act on both forms at different rates.
(3) They may assimilate first one form and then commence on the optical isomer.

Frankland[1] in 1891 showed that *B. ethaceticus* could be induced to act on both forms of calcium glycerates, whilst Fischer obtained assimilation of *l*-glucose as well as the ordinary *d*-glucose by yeast when the artifice was adopted of adding small quantities of the *l*-isomer from time to time.

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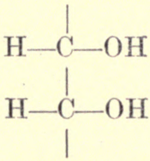
[1] *T. J. Chem. Soc.*, 1893, **63**, p. 1419.

Ethoxysuccinic acid was first resolved by the use of *Penicillium glaucum* (*l*-form destroyed) in 1893 by Purdie and Walker, whilst Le Bel (1899) claimed the resolution of

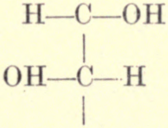
by the same means. Le Bel's experiments, however, could not be confirmed.

Bertrand, in 1893, utilised the sorbose bacterium as diagnostic of the configuration of certain polyhydric alcohols, noting that fermentation of a sugar was dependent on the presence of the grouping



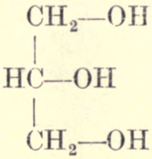
$$\begin{array}{c} | \\ \mathrm{H—C—OH} \\ | \\ \mathrm{H—C—OH} \\ | \end{array}$$

in the α-position. Sugars with the grouping



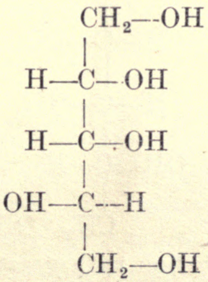
$$\begin{array}{c} \mathrm{H—C—OH} \\ | \\ \mathrm{OH—C—H} \\ | \end{array}$$

in the α-position are not attacked. Thus glycerol,



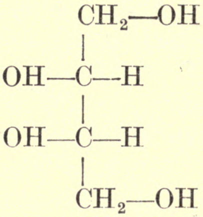
$$\begin{array}{l} \mathrm{CH_2—OH} \\ | \\ \mathrm{HC—OH} \\ | \\ \mathrm{CH_2—OH} \end{array},$$

and *l*-arabitol :



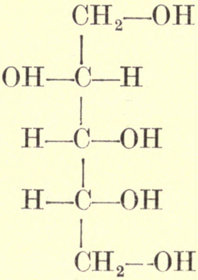
$$\begin{array}{c} \mathrm{CH_2—OH} \\ | \\ \mathrm{H—C—OH} \\ | \\ \mathrm{H—C—OH} \\ | \\ \mathrm{OH—C—H} \\ | \\ \mathrm{CH_2—OH} \end{array},$$

undergo oxidation, whereas *l*-xylitol :



$$\begin{array}{c} \mathrm{CH_2{-}OH} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{CH_2{-}OH} \end{array},$$

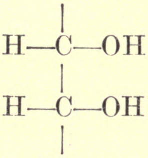
and dulcitol :



$$\begin{array}{c} \mathrm{CH_2{-}OH} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2{-}OH} \end{array},$$

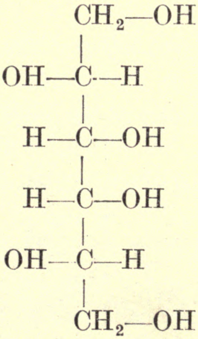
are not.

E. Fischer was in this way able to distinguish between *d*-galactose and *d*-talose, but the dependence of the fermentation process on the presence of the groupings



$$\begin{array}{c} | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \end{array}$$

in the *a*-position to the $CH_2{\cdot}OH$ grouping in the higher saccharoses is not so marked since *d*-galactose,



$$\begin{array}{c} \mathrm{CH_2{-}OH} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{CH_2{-}OH} \end{array},$$

undergoes slow fermentation with yeast.

ANTIENZYMES

We have already noted that, although enzyme activity is by no means specific in cases of hydrolysis or oxidation, yet this peculiar specificity of enzyme catalysis is much more marked when they are employed for accelerating hydrolytic or oxidation processes in optically active compounds. The organisms, however, even in this case, either elaborate a new enzyme, or a single enzyme is able to attack the more resistant isomeride after prolonged exposure to it. As we shall have cause to observe also when discussing the reaction kinetics of enzyme action, some form of combination between enzyme and substrate is the only logical interpretation of these results. Enzyme activity is governed by the capability of the enzyme to combine with the substrate; the form of combination, whether adsorptive or chemical, cannot definitely be settled, but it appears highly probable that adsorption precedes chemical reaction, and that although enzyme activity may be occasioned by the mere presence of adsorbed catalyst, yet the reaction proceeds more rapidly when actual chemical combination takes place between catalyst and substrate. Such chemical combination appears only possible in the carbohydrates when there exists a definite configuration of certain groupings in the carbon chain.

In such cases, the intermediate compounds enzyme-carbohydrate or enzyme–protein are unstable, easily undergoing hydrolysis or oxidation as the case may be, but there exists also a class of substances in which such combination is not only, as is to be expected, entirely specific for the enzyme, but also remarkably stable; under such conditions, addition of this substance, the anti-enzyme to the enzyme, will form the complex enzyme-antienzyme resulting in an entire loss of enzyme activity.

Antienzymes may be produced as in the case of antitoxins, also products of bacterial activity, by the injection of small doses of enzymes into the blood stream. Many normally occur in the human body, and are of physiological interest. Although a great number of antitoxins have been isolated, the production of true antibodies for the enzymes is not yet well established, thus W. Bayliss[1] could not confirm the existence of Beitzke and Neuberg's[2] anti-emulsin. Heden[3] assumes that antibody effects in sera are caused by adsorption of the enzyme by colloidal bodies therein, and in many cases it can be shown that the observed results are occasioned by the effects of the environment in repressing catalytic activity.

Emphasis, however, must be laid on the fact that the complex enzyme-antienzyme need not necessarily be a molecular compound; we have no reason to suppose that when chemical reaction occurs between two colloids or between a colloid and a substance in solution each molecule contained in the physical individuum, the colloid particle, must necessarily undergo chemical reaction. It will suffice, so far as chemical or physical reactivity of the enzyme is concerned, that only the superficial molecules on the physical individuum should react with the antitoxin, or in certain cases, where the molecules contained in the individuum are small and the intramolecular space or network is correspondingly enlarged, the active layer of superficial molecules (sometimes a few molecules thick) must be caused to react.

This interpretation of the neutralisation of toxin by antitoxin, enzyme by antienzyme, offers a ready solution to the Danysz effect. Danysz noted that if 5 units of toxin were neutralised with 5 units of antitoxin, the unit in each case being arbitrary and correspondingly equivalent, complete neutrality so far as toxicity was concerned was obtained, a result to be expected. If, on the other hand, the 5 units of antitoxin were added one at a time, over-neutralisation would be found in the resulting solution, and a small amount of toxin would be found necessary to correct for toxic neutrality; a fact incompatible with ordinary chemical reactions.

THE REACTION KINETICS OF ENZYME ACTION

The influence of temperature on enzyme catalysis.—Enzyme catalytic processes are characterised by the extremely narrow limits within which their catalytic influences are manifested. With increasing temperature, the activity

[1] *J. Physiol.*, 1912, **43**, 455.

[2] *Virchow's Archiv*, 1906, **183**, 169.

[3] *Biochem. J.*, 1906, **1**, 495.

increases to a maximum and then more or less rapidly sinks to zero.

The position of the maximum varies with the nature of the enzyme, those of vegetable origin usually operating best at 25° (Papain appears to be exceptional in that its optimum temperature is above 40°), whilst enzymes of animal extraction have a maximum activity of about 38°, certain enzymes[1] derived from cold-blooded animals act best at 15°.

Nearly all enzymes are practically inert at 0°, although it may be noted that a slight activity is frequently noted at lower temperatures, viz., −9° to −14°. One of the authors had occasion to examine a piece of frozen meat preserved at − 5° for eighteen years. No lipoclastic changes had taken place, but the extractive nitrogen figure was some three times that normally obtained in freshly-killed meat, indicating a certain amount of proteoclastic activity. At 60°, most enzymes undergo fairly rapid destruction, decomposition being already noticeable at the optimum temperature, and are practically instantaneously destroyed by boiling water; certain exceptions are found among the toxins which exhibit similar characteristics to the enzymes and anthrax spores will resist boiling water for no inconsiderable period, but are ultimately destroyed by such treatment.

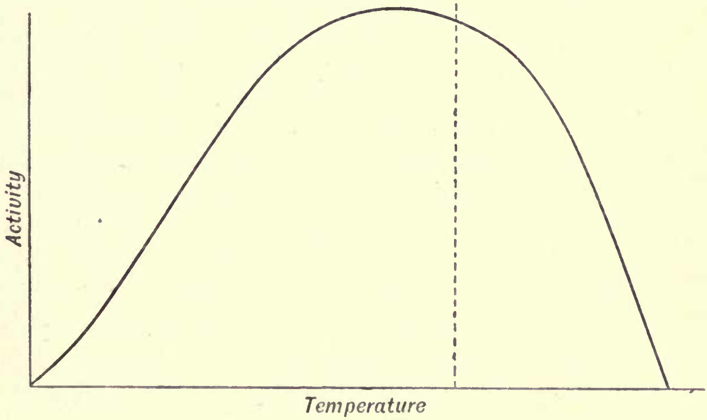


FIG. 21.

The temperature-coefficients of enzyme actions are as a

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[1] Cohen, "Organic Chemistry," p. 348.

rule high, and approximate to those of usual chemical reactions.

In considering the reason for this somewhat unexpected result, when, as we have already noted, we would naturally expect the somewhat lower values obtained for the temperature-coefficients of adsorption or diffusion processes, the following observations may be made.

The primary reaction between the substrate and the enzyme resolves itself into a heterogeneous reaction in which one reactant consists of a number of micro-heterogeneous surfaces. We may assume either that chemical reaction proceeds with very great velocity at the surfaces of contact—the velocity of the reaction will then be governed by the diffusion rate and the temperature-coefficient will be low, or that the chemical reaction proceeds with a very slow velocity and that the period required for diffusion processes to complete themselves is negligible in comparison; under these conditions the temperature coefficient of the reaction will be similar to ordinary chemical reactions. From observed results on the temperature-coefficient measurements, this latter position is frequently approximated to, but in certain others the rate of chemical reaction appears comparable with that of diffusion, and intermediate and unconstant values for the temperature-coefficient are arrived at.

It must also be noted that diffusion limitations are imposed, not only on the surface of the catalytic colloid, but intra-diffusion rates must also be considered. The diffusion limitations imposed on heterogeneous catalytic systems are naturally more marked in macro-heterogeneous systems than in the micro-systems comprising enzyme action. In this latter case, Brownian movement goes far to compensate for this disadvantage of heterogeneous catalysis. Henri, on examination of certain enzyme actions, showed that $dv/d\theta$, the temperature-coefficient, was appreciably larger in solution than when the enzyme itself was immobilised on a gelatin plate in the solution of the substrate.

Influence of medium on enzyme action.—Enzymes generally exert their maximum activity in neutral ($P_{\dot{H}} = P_{OH'}$) solutions. Certain exceptions have already been mentioned, *e.g.*, rennet and pepsin are more active in slightly acid solutions; the activity of invertase goes through a maximum with rising hydrion concentration, whilst trypsin and lipase exert their optimum activity in weakly alkaline solutions. Starkenstein[1] claims that liver amylase is inert in the absence of neutral salts.

In the decomposition of hydrogen peroxide by amygdalin, the following curve (Fig. 22) illustrates the dependence of the activity on the reaction of the medium.

The increased activity of enzyme by the addition of certain electrolytes resembles the action of the addition of promoters to ordinary catalytic processes.

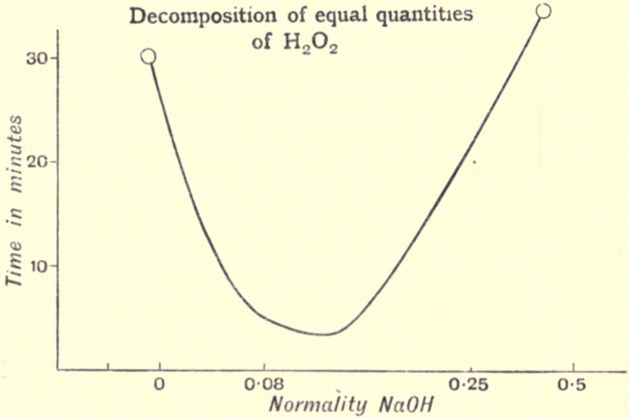

FIG. 22.

It is at once evident that since the activity of the enzyme varies in many cases with the hydrogen-ion concentration of the medium, those reactions in which a change of the acidity of the medium takes place will not exhibit a constant value for the velocity constant, but it will alter as the reaction proceeds, owing to the autocatalytic effect of the increase or decrease in concentration of the promoter. The autocatalytic effects observed where the catalyst is increased or decreased in concentration during the reaction is naturally different from those cases where a change in promoter concentration is observed.

A good example is found in the proteoclastic enzyme trypsin, which forms several amido-acids as a result of protein

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[1] *Biochem. Zeitsch.*, 1910, **24**, 210.

hydrolysis. Robertson[1] and Schmidt[2] have followed the change in hydroxyl-ion concentration during tryptic reactions and Bayliss[3] has actually obtained a solution acid to litmus.

The function of salts as promoters.—We have already noted that the primary process of enzyme action is undoubtedly an adsorption of the substrate by the enzyme to form a complex. Since the enzymes themselves are colloidal and the substrates also frequently are, we are confronted with the problem of determining the influence of small quantities of added electrolytes on the mutual adsorption of two colloidal systems. It appears that the enzymes themselves are isoelectric in water, *i.e.*, possess no electric charge, the small positive charge on pepsin and negative charge on pancreas enzymes being attributable to the presence of dialysable impurities.

It therefore follows that both $H^{\cdot}$ and OH', which are present in equal quantities in the solution, are equally diffusible within the colloid; on the addition of excess $H^{\cdot}$ or OH' (acid or alkali) the enzyme will take up an excess of the superabundant ion and assume a positive or negative charge with respect to the solution, thus pepsin can be given a positive charge in acid solutions and a negative one in alkaline solutions. We may, of course, alternatively suggest that the enzymes are amphoteric in character and form acids or bases depending on the reaction of the medium; no chemical evidence, however, can as yet be advanced to support this view.[4]

It is evident that mutual adsorption between two colloidal systems will proceed at a greater rate as the electrostatic difference of potential between the colloids increases, although mutual adsorption will undoubtedly occur when no difference of potential exists owing to the contact caused by Brownian movement and chemical reaction taking place at the surface of contact. If the rates at which hydrion diffuses into or is adsorbed by the enzyme differs from that of the substrate, the enzyme will take on a charge positive relative to the substrate and electrostatic attraction will ensue, resulting in an increase of the velocity of change. Hydrion and hydroxylion are the most effective electrical promoters on account

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[1] *J. Biol. Chem.*, 1908, **5**, 31.

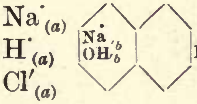
[2] *Zeitsch. physiol. Chem.*, 1910, **67**, 314.

[3] "The Nature of Enzyme Action," p. 88.

[4] See Michaelis, *Biochem. Zeitsch.*, 1913, **49**, 333.

of their high ionic mobility and diffusive powers, but neutral dissociating salts such as sodium chloride may prove effective, *e.g.*, in the case of amylase, on account of the difference in adsorptive powers or the selectivity in intracolloidal diffusivity of other anions or cations between enzyme and substrate.

It appears from these considerations that the optimum $P_{\dot{H}}$ should vary when the same enzyme is used with the nature of the substrate. We can calculate from Donnan's theory[1] the ideal case when a colloidal particle containing pure water is placed in, say, a weak saline solution, and further assume that the colloid is permeable to the sodion and absolutely impermeable to the chlorion. The sodion will commence to pass through and as a result OH′ ions will also commence to diffuse from the outer liquid through the colloid into the interior. At the equilibrium state we will be left with the following distribution of the ions.



micelle of the colloidal enzyme.

Writing down the virtual work required to move δn mols. of sodion from the solution to the micelle and δn mols. of hydroxylion in the same direction, the first is equal to

$$\delta n \,.\, RT \,.\, \log \frac{Na^{\cdot}_a}{Na^{\cdot}_b}$$

and the second to

$$\delta n \,.\, RT \,.\, \log \frac{OH'_a}{OH'_b}.$$

The osmotic work done is therefore equal to

$$\delta n \,.\, RT \,.\, \log \frac{Na^{\cdot}_a}{Na^{\cdot}_b} + \delta n . RT . \log \frac{OH'_a}{OH'_b}$$

and can be equated to the change in electrical energy if we assume that the colloid liquid potential difference is $\delta\pi$

then $$F\delta\pi\delta n = \delta n \,.\, RT \,.\, \log \frac{Na^{\cdot}_a}{Na^{\cdot}_b} + \delta n \,.\, RT \,.\, \log \frac{OH'_a}{OH'_b}$$

$$\therefore \delta\pi = \frac{RT}{F}\left(\log \frac{Na^{\cdot}_a}{Na^{\cdot}_b} + \log \frac{OH'_a}{OH'_b}\right)$$

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[1] *Zeitsch. Elektrochem.*, 1911, **17**, 572.

Further, we have noted that $\mathrm{Na}^{\cdot}_b = \mathrm{OH}'_b$ also $\mathrm{H}^{\cdot}_a = \mathrm{OH}'_b$ and if K be the value for $(\mathrm{OH}')\,(\mathrm{H}^{\cdot})$ in water $\mathrm{OH}'_a = \dfrac{\mathrm{K}}{\mathrm{H}^{\cdot\,2}_a}$.

$$\therefore \delta\pi = \frac{RT}{F}\left(\log \frac{\mathrm{Na}^{\cdot}_a}{\mathrm{H}^{\cdot}_a} + \log \frac{K}{\mathrm{H}^{\cdot\,2}_a}\right)$$

giving the potential difference in terms of the sodion and hydrion concentrations of the external solution.

In reality, of course, the process is more complicated owing to the fact that the micelle walls are permeable to both anion and cation of the salt, but the rates of permeation are different, thus permitting excess of one ion to pass through with its attendant hydrion or hydroxylion and thus establish equilibrium with partial hydrolysis of the salt. Excess of salts naturally cause the colloids to become unstable and precipitation or salting out occurs.

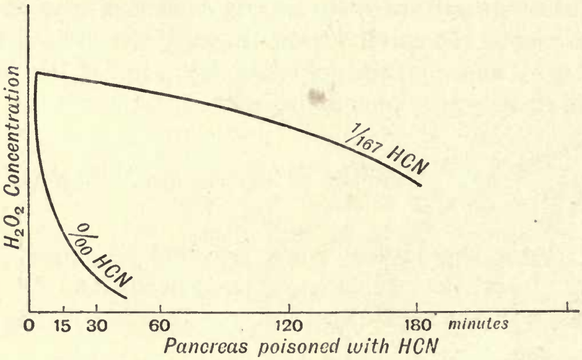

FIG. 23.

Enzyme poisons.—Enzyme catalysts are particularly sensitive to certain poisons such as hydrocyanic acid, hydrogen sulphide, mercuric chloride, and iodine. This fact forms the basis of the practical methods of food preservation in which enzyme activity is prevented by the addition of small quantities of preservatives. G. Bredig[1] cites a case of poisoning of pancreas catalase by the addition of 1/167th of 1 per cent. HCN; the effect of this addition on the rate of catalytic decomposition of hydrogen peroxide is observed from the above curves (Fig. 23).

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[1] *Biochem. Zeitsch.*, 1907, **6**, 313

Sentier obtained the following approximate figures for the necessary concentration of poison to reduce the catalytic activity of thrombase by one half.

Poison.	Concentration.
HCN	$1:10^6$
H_2S	$1:10^6$
$HgCl_2$	$1:2{\cdot}5 \times 10^6$
I_2	$1:5 \times 10^4$

It appears probable that the enzyme is not the most sensitive constituent of the living cell, since in many cases it is possible to kill the organism without injuring the enzyme contained in it. Both organism and enzyme, however, are selective in action towards poisons, thus one can destroy the organism without injuring the enzyme, or *vice versa*, by suitable choice of poisons.

Experiments by one of the authors appear to indicate that in organisms containing several ferments, *e.g.*, the fermenting and saccharoclastic enzymes of the organisms allied to *Bacillus coli*, it is possible to destroy fractionally the enzymes one after the other in the living organism by suitable treatment with graduated strengths of poisons such as chlorine water.

The reaction velocity and influence of concentration.—The reaction velocity of enzyme actions has been carefully investigated in the case of many hydrolytic processes, notably by Bayliss,[1] who has examined the hydrolysis of albumin by trypsin, by Henri[2] and Duclaux[3] the inversion of cane-sugar by invertase; by Brown and Glendinning,[4] starch hydrolysis by diastase, and by F. Armstrong on lactase, maltase, and emulsin.

The reaction follows in general a monomolecular law and may be expressed by the equation:

$$-\frac{dc}{dt} = Km\,.\,C.$$

Where K is the velocity constant, m the concentration of enzyme and C the concentration of hydrolysable substance in a great excess of water.

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[1] "The Nature of Enzyme Action," p. 75.

[2] "Lois générales de l'action des Diastases," Paris, 1903.

[3] "Chimie Biologique," Paris, 1883.

[4] *J. Chem. Soc.*, 1902, **81**, 388.

If we assume that the active mass of the enzyme remains constant during hydrolysis, then :

$$-\frac{dc}{dt} = (Km)C$$

or
$$\log_e \frac{C_1}{C_2} = Km(t_2 - t_1)$$

(i)
$$\therefore \quad K = \frac{1}{m(t_2 - t_1)} \log_e \frac{C_1}{C_2}.$$

Values of K as calculated from this equation, however, are never constant and either rise or fall with the time. These discrepancies may be accounted for by the following considerations.

We have already noticed that a primary combination of enzyme and substrate to form an adsorption complex precauses all enzyme activity. When only small quantities of enzyme are present and relatively large quantities of substrate to be hydrolysed, since the concentration of the complex (mC) is so much less than C, the concentration of the substrate will remain constant over very wide intervals of time, thus, since hydrolysis is governed by the complex concentration :

(ii)
$$-\frac{dc}{dt} = (KmC) = K',$$

or the quantity hydrolysed will be proportional to the time and independent of other factors.

F. Armstrong obtained the following figures[1] for the amount of milk-sugar hydrolysed in forty-six hours by the addition of a very small quantity of lactase.

Initial percentage concentration milk-sugar.	Quantity hydrolysed per forty-six hours.
10	2·22
20	2·18
30	2·21

Similar observations were made by Duclaux on the inversion of cane-sugar by invertase.

Not only does the enzyme combine with the substrate,

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[1] See Bayliss, "The Nature of Enzyme Action," p. 80.

but it is frequently adsorbed by the products of the hydrolysis. If, as appears to be the case, enzyme activity only follows on primary adsorption of the substrate by the enzyme, then since enzyme reactions are strictly reversible, it necessarily follows that the enzyme should exert some adsorptive power for the products of hydrolysis. Further, we have noted that the enzyme itself, even below the optimum temperature, gradually loses its activity, consequently we must expect the value of the enzyme concentration gradually to sink during the progress of a reaction for these two causes, generally expressed by the following equation :

$$-\frac{dm}{dt} = a(\delta c_1) + \beta f(\theta)$$

where a and β are constants, δc_1 the quantity of the hydrolysed substrate, formed in time δt, and $f(\theta)$ the temperature factor expressing the instability of the enzyme.

We would thus expect the values of K as determined from (i) gradually to rise with the time, as was found by Henri for the conversion of cane-sugar by invertase, who obtained the following values :

Time in minutes.	Velocity constant.
66	0·00058
168	0·00064
334	0·00072
488	0·00077
696	0·00085
1,356	0·00097

Other influences may, on the other hand, cause the observed values of K to fall with the time, thus the synthetic action of the enzyme on the hydrolysed substrate may convert the simple equation even in the presence of large quantities of water into an opposing reaction having a separate value of K for both forward and reverse change according to the equation :

$$\frac{dc}{dt} = K_1(a - C) - K_2C^2,$$

or the products of hydrolysis may act as promoters or inhibitors to the catalytic enzyme by changing the hydrion concentration of the solution, as was noticed by Bayliss in the action of trypsin on albumin, where he obtained values of K as follows :

Time in minutes.	K
10	0·0079
20	0·0046
30	0·0032
40	0·0022
50	0·0016
70	0·0009
90	0·0007

The enzyme substrate complex.—The development of the theory of enzyme action centres around the hypothesis that enzyme and substrate form some sort of complex before the substrate undergoes the catalytic change induced by the enzyme. Observations on the influence of temperature on the stability of enzymes without and with the addition of substrates and the previously recorded work on the reaction velocity of enzyme action support this view.

Further, a study of the selective nature of certain enzyme actions, and especially the existence of antienzymes, point to the existence of some form of chemical combination between enzyme and substrate.

If a given quantity of enzyme ϵ be added to a solution of substrate of concentration S, some form of equilibrium must eventually be arrived at between the reactants

$$\epsilon + S \rightleftarrows \epsilon S.$$

We may argue that the preliminary reaction is one of pure absorption and that chemical reaction is secondary and independent of the adsorption process, equilibrium will then obtain according to the usual adsorption formula :

$$(S\epsilon) = K[S \,.\, \epsilon]^{1/n}$$

where K and n are constants.

Whilst if the primary reaction is purely chemical, equilibrium will be established in accordance with mass action, and since the complex may be regarded as the result of the combination of a very weak acid and base, the equilibrium equation is expressed by :

$$S \,.\, \epsilon = K(\epsilon S)^2$$

where K is a constant.

It is evident that for values of $1/n$ approaching $1/2$ it is not easy to distinguish between the two possible modes of reaction by a study of equilibrium conditions. This is well emphasised in the investigations on the toxin antitoxin reactions which are identical in relation with the enzyme antienzyme reactions.

The following figures[1] show the discrepancies observed between calculation and observation in two typical toxin antitoxin reactions :

(*a*) Assuming the equilibrium to be established according to the equation

$$S \,.\, \epsilon = K(S\epsilon)^2.$$

In the combination of lysin and antilysin the following figures indicate the observed and calculated amounts of free lysin after adding n parts of antilysin to 1 part of lysin :

$$K = 0{\cdot}115.$$

	Free lysin.	
n	Observed.	Calculated.
0	100	100
0·1	70	66
0·2	36	38
0·3	22	23
0·5	10·1	10·4
0·7	6·1	6·3
1·0	4·0	4·0
2·0	1·8	1·9

(*b*) Assuming the equilibrium to be established according to the adsorption isotherm equation, Biltz has calculated the reaction diphtheria-toxin antitoxin equilibrium values where :

$$K = 177 \text{ and } 1/n = 0{\cdot}102.$$

Free toxin in solution.	Toxin antitoxin complex.	
	Observed.	Calculated.
1·2	197	180
11·1	222	230
28·0	240	255
49·8	251	270
57·6	283	275
72·8	290	280

It will be noted that experimental errors are sufficiently great

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[1] See Arrhenius, "Immunochemie," p. 131.

as to minimise the value of such equilibrium methods of diagnosis.

Michaelis[1] assumes that the enzyme forms a definite compound with the substrate, thus in the action of invertin on sucrose he postulates the following sequence of chemical actions:

Invertin + sucrose → Invertin sucrose compound →
dextrose + lævulose + invertin.

Although invertin can combine with the products of hydrolysis, Michaelis considers such compounds to be inactive and only serve to render less invertin available for hydrolysis; he further shows that the rate of decomposition of the invertin sucrose compound follows a unimolecular law, and that the dissociation constant of the sugar ferment complex (K) as deduced from the equation:

$$\frac{dS}{dt} = K\frac{\phi S}{S + k},$$

where K is a constant, S the concentration of the sugar, ϕ that of the ferment, is equal to 0·0167. In spite of the ardent support given by Arrhenius to the chemical theory, a considerable body of opinion favours the view that absorption is in reality the true mechanism of the process.

INORGANIC FERMENTS

The term "inorganic ferments" was applied by Bredig[2] to colloidal metallic sols prepared by electrical dispersion methods.

Ritter and H. Davy first made use of cathodic dispersion methods for the preparation of metallic sols, which method has now been supplanted by those of Bredig and Svedberg.[3]

For the preparation of pure hydrosols the electrical methods

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[1] *Biochem. Zeitsch.*, 1913, **49**, 333; 1914, **50**, 1.

[2] *Zeitsch. physikal. Chem.*, 1899, **31**, 258; 1901, **37**, 1, 323; *Ber.*, 1904, **37**, 798; *Zeitsch. Elektrochem.*, 1908, **14**, 51; "Anorganische Fermente," Leipzig, 1901.

[3] "Methoden zur Herstellung Kolloider Losungen," Dresden, 1909.

offer certain advantages over chemical processes, such as reduction with phosphorus (Faraday), formaldehyde (Zsigmondy), hydrazine (Gutbier), acrolein (Castoro) or protalbinic and lysalbinic acids (Paal), in that impurities which may act as protective colloids or as precipitating electrolytes are entirely eliminated. Reduction with hydrogen[1] or carbon monoxide[2] produces purer sols than the previously mentioned chemical reduction processes, but are not so good as the methods of electrical dispersion.

The following diagrams illustrate Bredig's and Svedberg's methods for the preparation of hydrosols and organosols of the metals.

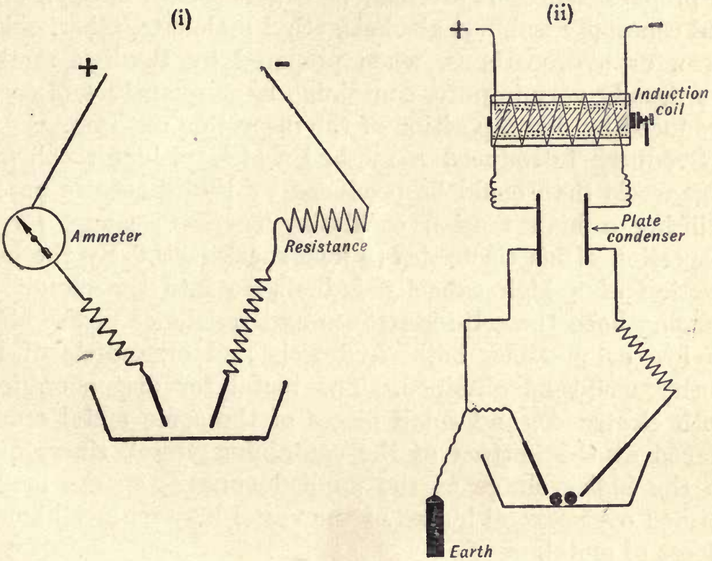

Fig. 24.

In Bredig's method of preparation, an electric arc (4—10 amperes at 50 to 220 volts) is struck between two thin wires of the metal under the liquid. The wires should not exceed 2 mm. in diameter and the optimum arc gap is usually only one or two mm. in length.

Silver, gold, platinum, and iridium sols can easily be pre-

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[1] Kohlschütter, *Zeitsch. Elektrochem.*, 1908, **14**, 49.

[2] Donau, *Monatsh.*, 1905, **26**, 525; 1906, **27**, 71.

pared by this method. The addition of a trace of alkali yields a better sol, but, for many purposes, electrolytes must be entirely eliminated. The process is in reality one of cathodic dispersion, since the anode frequently gains somewhat in weight during sol formation. For metals which are somewhat easily oxidisable, such as lead, cadmium, and copper, the water must not contain any oxygen, and the sol should be prepared in a hydrogen or nitrogen atmosphere.

Metals such as zinc or iron yield hydroxides when attempts to prepare hydrosols are made. Organosols in methyl, ethyl, and especially isobutyl alcohols, ethyl malonate, ether, chloroform, or hydrocarbons, when prepared by Bredig's method, are usually very impure, containing large quantities of carbon produced by decomposition of the dispersion medium.

Svedberg introduced a method which yielded much purer organosols than could be produced by the direct arc process, utilising a high tension oscillating spark discharge for the dispersion of his electrodes (6 inch spark coil). By the introduction of a high capacity inductance into the circuit and keeping both the self-inductance and resistance of the circuit as low as possible, both hydrosols and organosols of high purity could be obtained. The metal for dispersion forms both electrodes, and small pieces of the same metal may be placed at the bottom of the containing vessel, since, owing to the high voltage of the applied current, sparks may be formed over several inches of the vessel between neighbouring pieces of metal.

Less than 2 per cent. of carbon is usually introduced when an organosol, *e.g.*, isobutyl alcohol sol is prepared in this manner. By slight modification of Svedberg's method even non-metals of poor conductivity may be dispersed. Svedberg has prepared organosols of such elements as sulphur, phosphorus, carbon, and silicon, as well as of certain minerals, such as copper sulphide. A high degree of dispersity has readily been attained.

The hydrosols thus prepared are usually negatively charged, although certain metals, especially iron and bismuth, are positive, owing, doubtless, to the presence of hydroxides, which in the sol form are usually positive.

The differences of potential between sol and dispersion medium are small. Thus, Burton[1] gives the following figures :

Dispersion medium.	Sol.	E in volt.
Ethyl malonate	Pt	− 0·054
	Au	− 0·033
Ethyl alcohol	Ag	− 0·040
	Pt	+ 0·024
Methyl alcohol	Zn	+ 0·015
	Pb	+ 0·046

The average electric charge on a particle of silver sol is, according to the same investigator, about $2{\cdot}8 \times 10^{-2}$ electrostatic units, or on one gram-equivalent of silver in the dispersed state only 4 per cent. of the charge on a gram-equivalent when ionised. Both charge and sign naturally vary when electrolytes are added to the dispersion medium and, as in other colloidal systems, the usual phenomena of precipitation and adsorption are noticed.

In preceding pages we have already noted the application of colloidal metals to catalytic operations, but the striking resemblances of the colloidal metallic sols to organo-enzymes are most convincingly demonstrated by their behaviour in the catalytic decomposition of hydrogen peroxide, which subject has been minutely investigated by Bredig and his co-workers.

Very small concentrations of the metal sol are able to influence catalytically the rate of decomposition of hydrogen peroxide solutions. Thus, Bredig obtained the following values for a minimum observable catalytic influence.

Metal sol.	Dilution 1 gram atom per
Pt	$70{\cdot}10^6$ litres
Pd	$26{\cdot}10^6$
Au	$1{\cdot}10^6$

Some colloidal metallic oxides were also observed to have a feeble catalytic influence.

The decomposition of the hydrogen peroxide follows that of a reaction of the first order,

$$\frac{dc}{dt} = KmC$$

or

$$K = \frac{1}{m(t_2 - t_1)} \log \frac{C_1}{C_2}$$

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[1] *Phil. Mag.*, 1904, **6**, 7425 *et seq.*

where m = concentration of sol, C the peroxide concentration, but, as was noted in the case of enzyme action, the values of K are only approximately constant.

The chief causes for irregular results are due to :

(*a*) Instability of the metal sol in warm dispersion media. The effect of heat is to precipitate the sol in a metallic condition ; elevation of the temperature hastens precipitation, but also accelerates the velocity of decomposition of the hydrogen peroxide ; consequently the velocity-temperature curve passes through an optimum point as in the case of enzymes (see p. 373).

(*b*) Destruction of the metal sol by hydrogen peroxide. The experiments of Loew and Senter indicated that ordinary catalases capable of accelerating the decomposition of hydrogen peroxide were actually destroyed by the reagent. McIntosh extended his observation to the inorganic ferments. It was shown that colloidal silver was rendered soluble by the hydrogen peroxide.

A high dispersivity in the sol is naturally a desirable feature for enhanced activity, as, under these conditions, the maximum surface per unit mass of substance is obtained and, at the same time, both the increase in the diffusivity and in the Brownian movement permit of a greater frequency of contact.

This increase of Brownian movement with increase in dispersivity is well exemplified in the following figures obtained by Zsigmondy for gold sols :

Diameter in $\mu\mu$	Amplitude in μ
6	>10
10	3 – 4
35	1 – 7.

How far ultimate subdivision from $5\mu\mu$, the lower limit of the ultramicroscope, to molecular dimensions $0{\cdot}0002\ \mu$ increases the catalytic activity is uncertain, since no method of size measurement for these amicrons has yet been proposed.

Ernst[1] adopting Henri's artifice[2] of fixing platinosol by means of gelatin, conclusively showed the enhancement of activity of the sol, due to Brownian movement of the sol particles in the solution.

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[1] *Zeitsch. physikal. Chem.*, 1901, **37**, 477.

[2] See page 374.

Another point of resemblance of the inorganic ferments to enzymes is found in their remarkable sensitivity to activators and catalyst poisons.

The catalytic decomposition of hydrogen peroxide is accelerated by the addition of a small quantity of hydroxyl ions in the form of a base. The following curve illustrates the variation in activity of a platinosol solution in the decomposition of peroxide with an increase in alkalinity :

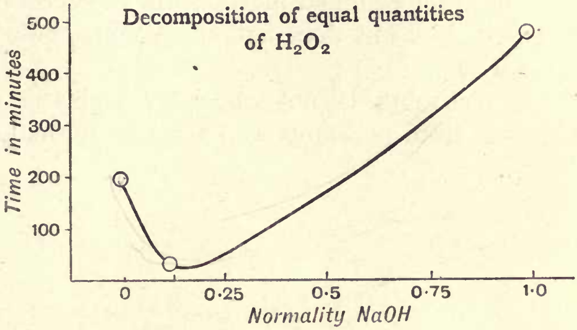

FIG. 25.

The resemblance of this form of curve to that cited on p. 375 is most marked.

Bredig's values for the inhibiting or poisoning influence of small quantities of hydrocyanic acid on platinosol are shown in the following curves :

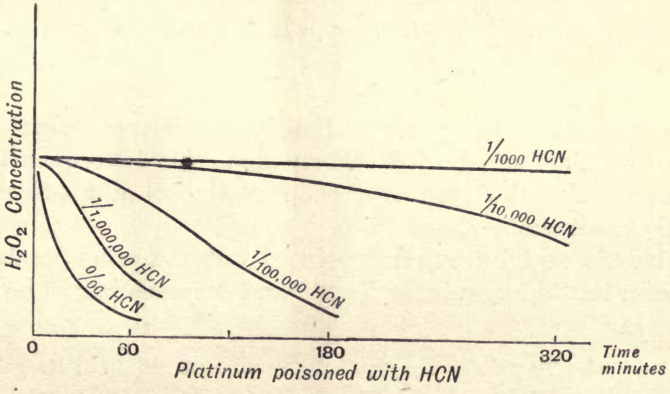

FIG. 26.

whilst the following concentration of poisons can be detected by their inhibiting influence on the decomposition of peroxide of hydrogen by platinosol.

Poison.	Concentration.
HCN	$1:20\cdot10^6$
ICN	$1:3\cdot10^6$
I_2	$1:7\cdot10^6$
$HgCl_2$	$1:2\cdot5\cdot10^6$ [1]

The action of carbon monoxide is an interesting one. It is an active poison for colloidal platinum in the decomposition of hydrogen peroxide, but does not affect manganese dioxide or organic catalysts.

Frequently, poisoning is not absolute, and the catalyst is able to recover from poisoning and exert its normal activity once more. Bredig made the interesting observation that platinum poisoned with carbon monoxide is frequently more active, after its recovery, than platinosol not subjected to this treatment.

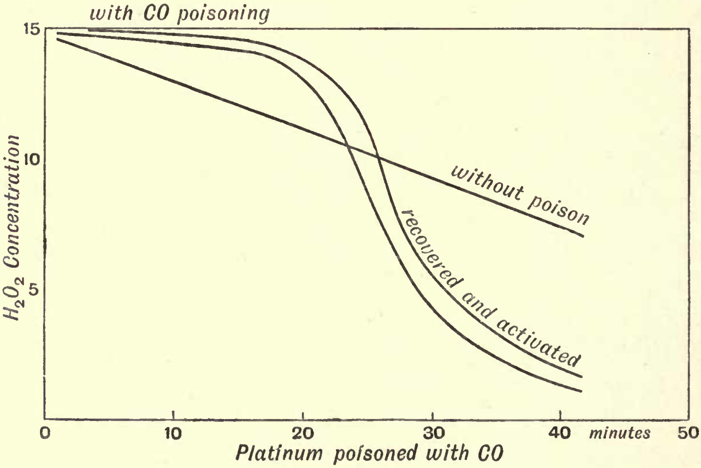

FIG. 27.

Kastle and Lövenhart[2] pointed out tha tthe analogy between the "inorganic ferments" and enzymes cannot be pressed too far.

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[1] See also Titoff, *Zeitsch. physikal. Chem.*, 1903, **45**, 611; Raschig, *Chem. Zeit.*, 1907, **31**, 926, and Chapter 2.

[2] *J. Amer. Chem. Soc.*, 1903, **29**, 397.

The effect of poisons is also a case of selective action. Thus, hydroxylamine and potassium nitrate poison liver catalase, activate a silver sol and are without action on platinosol. It is to be expected, as is indeed the case, that the halides, cyanides, and sulphides should act as poisons for a silver sol owing to the formation of a definite insoluble film on the surface of the colloid particles. The poison itself, as in the case of iodine, may also exert a catalytic activity *per se.*

Bredig has attempted to carry the analogy between colloidal metals and enzymes still further, pointing out that the preparation of mercury sol or that of manganese dioxide by the addition of gold or hydroxyl ions is comparable to the transformation of a proenzyme into an enzyme. (See p. 358.)

In this connection the interesting cases of rhythmic or pulsating catalytic reactions may be mentioned. Ostwald[1] directed attention to the fact that the evolution of hydrogen from the solution of chromium in various solutions was not in a continuous stream, but came off in periodic bursts. If the volumes liberated per minute were plotted against the time a regular sinuous curve was obtained (Fig. 28).

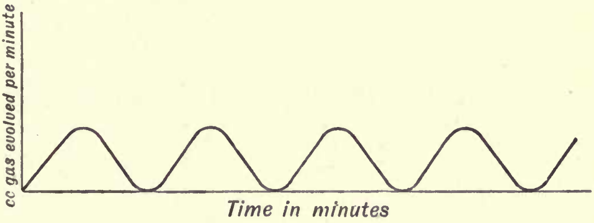

FIG. 28.

Bredig and Weinmayr,[2] in search of analogies with vital processes, were struck with the regular periodicity of this reaction, and compared it with that of a cardigram, or pulse curve. They subsequently noticed that a similar pulsating effect was obtained in the liberation of oxygen from hydrogen peroxide when exposed to a surface of clean mercury.

As in the case of the beating heart, the rate of liberation of oxygen from the mercury surface is influenced by the addition of small quantities of various substances, especially

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[1] *Zeitsch. physikal. Chem.*, 1900, **35**, 33.

[2] *Ibid.*, 1903, **42**, 601.

colloids, very small concentrations of hydrion or hydroxylion, and certain electrolytes such as sodium acetate or ammonium citrate. The extraordinary alteration in the character of the curve on the addition of a small quantity of ammonium citrate is well exemplified by the following example :

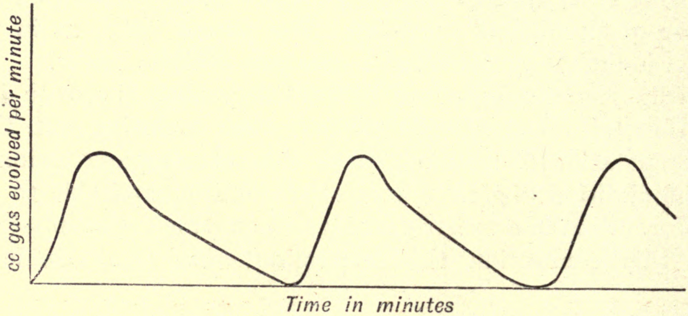

Fig. 29.

It will be noted that the simple sinuous character of the curve has been entirely destroyed.

CHAPTER XII

CATALYSIS IN ELECTRO-CHEMISTRY

CATHODIC REDUCTION

ELSEWHERE in this book we have noted the various applications of catalytic substances to accelerate the reduction of certain compounds in liquid media by means of gaseous hydrogen. With the aid of the electric current we have a means at hand of generating hydrogen *in situ* and can thus accomplish similar processes of reduction. In spite of the higher cost of hydrogen produced in this way, processes of electrolytic reduction are becoming increasingly important not only on account of the greater cleanliness of the operations, but also owing to the variety of products which can be obtained by a strict control of the reducing power of the hydrogen. It is in this strict control over the reducing power that the great merit of electrolytic processes lies.

During the course of electrolytic reduction, two catalytic reactions are to be observed : first, the specific action of the cathode material on the course of reaction, and, secondly, the effect of adding certain salts to the electrolyte in which reduction is proceeding. These two actions are frequently entirely distinct from one another, but in many cases mutual interference is so marked that distinction between phenomena occurring in the electrolyte and at the electrode surface is impossible.

The specific action of the electrode material.—Since, in electrolytic reduction, the hydrogen is produced at the surface of the cathode exposed to the electrolyte, we should expect that the course of the reactions proceeding in the adherent film would affect the nature of products obtained by reduction.

This is actually found to be the case. Thus, in the electrolytic reduction of nitrobenzene the quantity of the various products of reduction, nitrosobenzene, phenylhydroxylamine, amido-phenol, azoxybenzene, hydrazobenzene, benzidine, azobenzene, and aniline can be controlled at will by an alteration in the electrode reactions.

The primary electrode reaction, occurring at the cathode in the electrolysis of a dilute acid, is the discharge of hydrogen ions with the liberation of molecular hydrogen :

$$2H^{\cdot} \rightarrow 2H + 2\epsilon \rightarrow \overset{\uparrow}{H_2}.$$

When the molecular hydrogen evolved and the hydrogen ions in solution are in dynamic equilibrium, as found in an oxygen-hydrogen cell with perfectly reversible electrodes, the cathodic potential of the electrode in the electrolyte is given by the general formula developed by Nernst :

$$E = \frac{RT}{nF} \log_e \frac{H_2}{\dot{H}}$$

where F is the Faraday equivalent (96,540 coulombs per gram-molecule), n the valency of the discharged ion (in this case $n = 1$), H_2 and $\dot{H}$ the partial pressure and the ionic concentration of the hydrogen gas and the hydrion in solution respectively.

It follows that for the steady liberation of cathodic hydrogen from an electrolyte of unchanging composition a minimum potential difference between cathode and electrolyte must be applied, which cathodic potential has an important influence on the reducing power of the electrolytic hydrogen.

The investigations of Caspari,[1] Müller,[2] J. Tafel,[3] and Wilsmore[4] have shown that the value of E, the cathode potential derived from Nernst's formula, is not independent of the nature of the electrode material, as is assumed when conditions of dynamic equilibrium between the molecular, atomic and ionic hydrogen at or in the electrode surface are postulated. Such conditions of reversibility are only obtained

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[1] *Zeitsch. physikal. Chem.*, 1899, **92**, 30.

[2] *Zeitsch. anorg. Chem.*, 1900, **1**, 26.

[3] *Zeitsch. physikal. Chem.*, 1905, **50**, 641.

[4] *Ibid.*, 1900, **35**, 291.

when platinised platinum is used as cathode material and very low current densities are employed. All other metals give values for the cathode potential in excess of the calculated value for E. In the following table are given the magnitudes of this excess or over-potential (η) required to effect the liberation of molecular hydrogen at various metal surfaces :

Metal.	Over-potential in volt.	Metal.	Over-potential in volt.
Hg	0·78	Ni	0·21
Zn	0·70	Ag	0·15
Pb	0·64	Pt (bright)	0·09
Sn	0·53	Fe	0·08
Cd	0·48	Au	0·02
Pd	0·46	Pt (platinised)	0·005
Cu	0·23		

Thus the transformation of hydrion into molecular hydrogen requires $\frac{E + \eta}{E}$ times as much energy as is necessary at a perfectly reversible electrode. Eventually this excess energy reappears in the electrolyte as additional heat, since no subsidiary endothermic reactions have taken place.

It is evident that the various metals exert marked catalytic activity in the transformation of ionic into molecular hydrogen :

$$2\dot{H} \rightarrow 2H + 2\epsilon \rightarrow H_2$$

Since the discharge of hydrion proceeds at a definite rate for any given current intensity independent of the electrode material, the nature of the electrode material probably exerts a catalytic influence on the transformation of the discharged hydrion or atomic hydrogen into the molecular or gaseous form :

$$2H \rightarrow H_2.$$

The exact mechanism by which the metal exerts this catalytic activity is not fully explained, Roczkowski[1] suggested that over-potential was due, not to the non-catalytic nature of the metal in the reaction $2H \rightarrow H_2$, but to the effect of variable surface tension at the metal surfaces, thus assisting in the formation of a hydrogen film which could serve as the dielectric of a condenser formed by the metal electrolyte

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[1] *Zeitsch. physikal. Chem.*, 1894, **15**, 276.

surfaces.[1] Le Blanc and Möller[2] certainly obtained changes in the value of the over-potential by the addition of certain alkaloids to the electrolyte, but the changes in potential difference due to these causes are so insignificant as to discredit this hypothesis. Reichinstein[3] finds an explanation in the variable depth to which the deposited ions and the free gas molecules penetrate in the electrode surface, active electrode volume being thus the determining factor in over-potential production. With large electrode volumes, the tendency to interconversion of hydrion into molecular hydrogen is naturally less and the over-potential consequently higher. Pring, on the other hand,[4] carefully measured the effect of varying the metal film thickness of the electrode on the values of the over-potential and obtained results as follows :

Metal.	Minimum thickness for maximum values of η in cm.
Pt	4×10^{-6}
Cu	$3{\cdot}4 \times 10^{-3}$
Zn	$5{\cdot}5 \times 10^{-4}$
Ni	$1{\cdot}6 \times 10^{-2}$
Pb	$6{\cdot}6 \times 10^{-2}$

It will be observed that these values do not conform to Reichinstein's hypothesis, since, for example, zinc, which has a remarkably high η value, requires a thickness of metal considerably less than that of copper, which has a relatively low over-potential.

Bose[5] has modified Nernst's original view, in which the catalytic activity was entirely due to the occlusive power of the metal for hydrion, atomic hydrogen, and molecular hydrogen, by postulating that the over-potential is due to the difference of velocity in transformation of ions in solution into gas ions and the transformation of gaseous ions into gas molecules.

It must be admitted that the gas solution theory is open to criticism, in that palladium, in which hydrogen can diffuse with the greatest ease, still exerts a considerable over-potential in solution. We may, on the other hand, assume that, in

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[1] See also Haber, *Zeitsch. Elektrochem.*, 1902, **8**, 539 ; *Zeitsch. physikal. Chem.*, 1904, **47**, 257.

[2] *Ibid.*, 1909, **65**, 226.

[3] *Ibid.*, 1910, **16**, 916.

[4] *Zeitsch. Elektrochem.*, 1913, **19**, 255.

[5] *Zeitsch. physikal. Chem.*, 1900, **34**, 701.

this special case, the immiscible solid solutions of palladium in hydrogen and hydrogen in palladium noted by Hoitzema have a different electrode electrolyte potential difference from the pure metal. Newbery[1] has extended the idea of unstable hydride formation in the case of palladium to all the elements, postulating the existence of certain unstable endothermic hydrides which are formed during the liberation of hydrogen at a metal surface.

The work of Bennett and Thompson[2] seems to indicate the temporary existence, at least, of atomic hydrogen. These investigators state that active or atomic hydrogen may actually reduce cadmium from solutions of cadmium sulphate, and even zinc from zinc oxide.

It is difficult to imagine, on Newbery's hypothesis, for example, why arsenious oxide is reduced to arsine only by the solution of strongly electropositive elements, *e.g.*, zinc in dilute acid. If the formation of the unstable zinc hydride to which both the over-potential and also the powerful reducing action of hydrogen disengaged at zinc cathode are due, can be brought about by hydrogen under low pressures as developed by zinc on solution in acids, then it is difficult to imagine why such compounds cannot be isolated under high pressures of hydrogen and why they should be so much more reactive than ordinary hydrogen.

All evidence points to the transitory existence of some very reactive form of hydrogen between the stages hydrion and hydrogen molecule probably as monatomic hydrogen atoms,[3] and that the phenomenon of over-potential is due to the catalytic activity of the metals in promoting the association to molecules. Doubtless, also, hydration and dehydration of the ions as well as the further association of molecules to gas bubbles will be influenced by the electrode material, but rather by the smoothness or roughness of that surface which considerably affects the surface tension values of gas films on the wet surface than by the actual nature of the electrode.

The work of Haber[4] has indicated that the cathode potential

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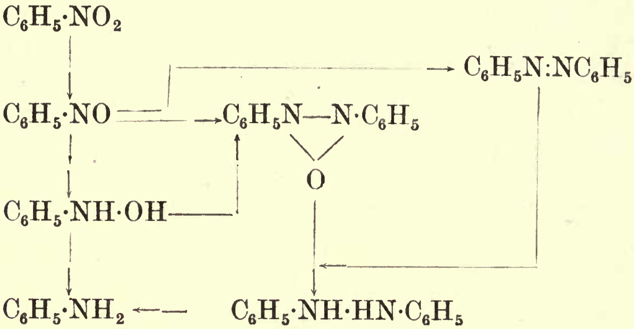
[1] *J. Chem. Soc.*, 1916, **109**, 1359.

[2] *J. Physical Chem.*, 1916, **20**, 296.

[3] Bancroft, *ibid.*, 396.

[4] *Zeitsch. Elektrochem.*, 1898, **4**, 506; *Zeitsch. physikal. Chem.*, 1900, **32**, 173, 271, and 1904, **47**, 263.

is the determining factor in the reducing power of electrolytic hydrogen.[1] By careful adjustment of this value he was able to isolate a great variety of compounds by the simple reduction of nitrobenzene in acid and alkaline electrolytes, according to the following scheme :



Utilising a 2 per cent. caustic soda solution as electrolyte, Löb and Moore obtained the following results :

Electrode material.	Over-voltage value.	Product.
Pt, Ni	0·15—0·23	Azoxybenzene.
Pb, Sn, Zn	0·64, 0·53, 0·70	Azobenzene.
Cu	0·46	Aniline.

The production of aniline, however, proceeds most rapidly in an acid electrolyte using a lead[2] or zinc cathode.[3]

The effect of addition agents to the electrolyte.—It will be noted that the catalytic activity of copper in the reduction of nitrobenzene to aniline is somewhat anomalous in view of its relatively small over-potential.

This point was investigated in detail by Chilesoti and Tafel,[4] who noted that metallic copper itself could rapidly effect the reduction of phenylhydroxylamine to aniline with the formation of cupric ions in solution. Thus, the copper electrode is functioning as a reducing agent, not only by reason of the liberation of hydrogen at the surface, but by actual solution and re-deposition of the metal :

$$Cu + 2\oplus \rightleftarrows Cu^{\cdot\cdot}$$

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[1] See also H. Goldschmidt, *Zeitsch. Elektrochem.*, 1900, **7**, 263 ; Nernst, *Zeitsch. physikal. Chem.*, 1904, **47**, 52, and Brunner, *ibid.*, 56.

[2] Löb, *Zeitsch. Elektrochem.*, 1898, **4**, 430.

[3] Elbs, *Chem. Zeit.*, 1893, **17**, 209.

[4] *Zeitsch. Elektrochem.*, 1901, **7**, 768 ; *Zeitsch. anorg. Chem.*, 1902, **21**, 289.

If ferrous salts be added to the electrolyte, a similar catalytic activity is noticed.[1] Thus, ferrous ions are oxidised to ferric ions by reduction of the phenylhydroxylamine, whilst the ferric ions thus formed are reduced at the cathode surface. In those cases where the cathodic potential is not sufficiently high to deposit the ions of the added salt, it is evident that unless precautions be taken to separate catholyte from anolyte a carrier action between anode and cathode may occur by which current may flow by means of the alternate oxidation and reduction of the polyvalent ion, thus :

$$\mathrm{Fe}^{\cdot\cdot} + \oplus \rightleftarrows \mathrm{Fe}^{\cdot\cdot\cdot}$$

This species of carrier action is frequently observed in electrochemical processes, *e.g.*, the presence of 0·1 per cent. of ferric salt, a very common impurity, in carnallite, is sufficient to reduce the current efficiency in the production of magnesium by more than 20 per cent. Carrier action is also frequently made use of in the electrolytic deposition of metals when divided cells are employed for electrolysis.

In the electro-deposition of copper, ferric sulphate is frequently employed as a leaching agent for roasted copper ores. A solution of cuprous and ferrous sulphate is thus formed from which copper is deposited in the cathode compartment of a cell, the spent liquor containing ferrous sulphate being returned through the anode compartment, where it is reoxidised to the ferric state preliminary to the treatment of a fresh batch of ore.

Tafel's experiments[2] on the electrolytic reduction of nitric acid to ammonia at lead and copper cathodes also indicate that copper exerts an anomalously high reactivity ; in this case electrolytic reduction of nitric acid, proceeds as far as hydroxylamine, whilst the second stage in the reduction process is performed almost entirely by the carrier action of the copper $\mathrm{Cu}^{\cdot\cdot} \rightleftarrows \mathrm{Cu} + 2\oplus$. A number of processes have been devised for accelerating the process of electrolytic reduction by these means, primarily using suitable cathode material to obtain the requisite cathode potential, and secondarily to promote the carrier action between electrode and electrolyte by the addition of metallic powder or salts of polyvalent elements.

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[1] Farnau, *J. physikal. Chem.*, 1912, **16**, 249.

[2] *Loc. cit.*

For example, copper or tin is used in the electrolytic reduction of *o*- or *p*-nitrotoluene to *o*- or *p*-toluidine[1] zinc in the preparation of hyposulphites,[2] mercury, vanadium, iron, or titanium, in the electrolytic reduction of indigo, titanium being frequently used in the reduction of quinine to hydroquinol.

In addition to the phenomenon of hydrogen overvoltage at the electrode and the possibility of ionic carrier action by partial solution and reprecipitation of the metallic electrode, the metal itself may exert a specific catalytic effect in the reduction process. It is reasonable to assume that since various metals exert a catalytic influence on the rate of combination of the discharged hydrogen, they may also affect the alternative reaction between the atomic hydrogen and the depolariser.

Thus, the reduction of chlorates to chlorides proceeds smoothly at an iron cathode, which is superior to platinised platinum in this respect. We may regard the catalytic activity of the iron to be evident in both the cathodic processes:

(*a*) The combination of atomic hydrogen to the molecular state:

$$2H \rightarrow H_2.$$

(*b*) The reduction of the chlorate ion by the atomic hydrogen:

$$2H + ClO'_3 \rightarrow ClO'_2 + H_2O$$
$$ClO'_2 + 2H \rightarrow ClO' \rightarrow Cl'.$$

In this case, the second process, the reduction of the chlorate, is accelerated by the iron, whilst, as shown by the overpotential value, the acceleration of the production of molecular hydrogen is distinctly inferior to that of platinised platinum.

The addition of colloidal materials to simple electrolytes as well as the use of complex electrolytes has marked effects on the nature of deposited metals and alloys; a discussion, however, of the mechanism by which the physico-catalytic influence of such additive agents on the rate of crystal growth

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[1] D.R.P. 117007/1900.

[2] See Jellinek, *Zeitsch. Elektrochem.*, 1911, **17**, 157 and D.R.P. 139567/1902.

in the deposited metals is effected is somewhat beyond the province of this volume, and the reader is referred to standard books on colloids and electro-chemistry for the full discussion of this matter.

ANODIC OXIDATION

In the discharge of anions such as OH′ and the halogens at metal surfaces, the phenomenon of over-voltage has also been observed. As a general rule, the over-potential values obtained at the anode are smaller than the corresponding cathodic values, or the catalytic activity of the anode material is consequently higher.

The following values were obtained by Coehn and Osaka in acid solution[1] and by Foerster in an alkaline electrolyte.[2]

Anode material.	Oxygen over-voltage,* (1).	Oxygen over-voltage,* (2).	Halogen over-voltage.		
			Cl_2	Br_2	I_2
Nickel	0·05 – 0·12	0·38 – 0·56	—	—	—
Cobalt	0·13	—	—	—	—
Iron	0·24	—	—	—	—
Platinised platinum ..	0·24	0·50 – 0·57	—	—	—
Lead peroxide ..	0·28	0·44 – 0·86	0	0	0
Smooth platinum ..	0·44	1·46	0·7	0·33	0

* See Müller, *Zeitsch. Elektrochem.*, 1902, **8**, 426; Yamasaki, *ibid.*, 1910, **16**, 321.

Foerster assumes the phenomena of anodic over-voltage to be due to the formation of an unstable oxide[3]; in the case of platinum a solid solution of the oxide PtO_3[4] in the metal is formed and a steady value for the over-potential is reached when equilibrium is established between oxide formation and decomposition.

The magnitude of the over-potential value is thus, according to Foerster, determined by the stability of the peroxide.

An application of the high anode over-potential value at a platinum surface is noted in the preparation of hypochlorites from a neutral aqueous solution of sodium

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[1] *Zeitsch. anorg. Chem.*, 1903, **34**, 86.

[2] *Zeitsch. Elektrochem.*, 1904, **10**, 714.

[3] *Zeitsch. physikal. Chem.*, 1904, **69**, 236; *Zeitsch. Elektrochem.*, 1910, **16**, 353.

[4] See Grube, *ibid.*, 1910, **16**, 621.

chloride. The electrode potential of chlorine at one atmosphere in normal sodium chloride solution is about − 1·37 volts, whilst that of oxygen is only some −0·82 volt. If it were not for the high over-potential value for oxygen rising to voltages greater than − 1·46 volts under a high current density and with a cold electrolyte, the preferential liberation of chlorine would not take place. The electrical efficiency of hypochlorite cells in which graphite electrodes are substituted for the more expensive platinum is usually somewhat low, part of the loss being due to the fact that the oxygen over-potential at a graphite anode is only sufficient to raise the electrode potential for oxygen discharge about 0·05 to 0·1 volt above that required for the liberation of chlorine. Dony Hénault[1] was able to effect the electrolytic oxidation of ethyl alcohol in sulphuric acid solutions either to acetaldehyde or to acetic acid by a rigorous control of the anode potential, $E_p = 1{\cdot}3$ volts in the former and 1·66 volts in the latter case.

The effect of addition agents to the electrolyte.—As in the cases of electrolytic reduction, the addition of catalytic salts to the anolytes with the view of increasing the rate of oxidation as well as the electrical efficiency of the process has been the subject of various investigations. Amongst the more important polyvalent metallic salts which have been used for this purpose are those of vanadium, uranium, thallium, manganese, chromium, cerium, and occasionally copper, as well as certain anions, such as the halides, especially the fluoride ion.

In the electrolytic oxidation of sulphuric acid suspensions of anthracene to anthraquinone, cerium sulphate, or chromic acid are usually employed as catalytic agents.

$$C_{14}H_{10} \rightarrow C_{14}H_8O_2$$
$$Ce_2(SO_4) \rightarrow Ce(SO_4)_2.$$

Cerium sulphate[2] is much more active than chromic acid, and may be employed in a cell with no diaphragm between anode and cathode. With chromic acid, on the other hand, a divided cell must be employed to prevent cathodic reduction of the chromic acid. Since the electrolytic regeneration of the

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[1] *Zeitsch. Elektrochem.*, 1900, **6**, 533.

[2] See Le Blanc, *Zeitsch. Elektrochem.*, 1900, **71**, 2903.

chromic acid does not usually keep pace with its reduction to chromium sulphate by means of the anthracene, the electrolyte containing the catalyst must be submitted to electrolytic oxidation from time to time.

In the preparation of per-salts, such as persulphates, percarbonates or perborates, the addition of a small quantity of a fluoride greatly enhances the yield.[1] In this case a high anode current density is usually employed with a metal exhibiting a high over-potential value for oxygen such as platinum ; the function of the fluoride ion is undoubtedly to assist in elevating the value of the anode potential owing to the high value of its discharge potential. In the Planté process of forming the positive electrodes of lead accumulator plates, the addition of small quantities of the chlorate ion considerably accelerates the rate of formation.

Manganese salts[2] are likewise frequently employed to accelerate processes of electrolytic oxidation in organic compounds, such as the conversion of aniline to quinone.

As in cases of electrolytic reduction, the nature of the anode material has a considerable influence on the yield, apart from the value of the oxygen over-potential or the effect of solution and reprecipitation of the metal.

Brand and Ramsbottom[3] noted that the oxidation of manganates to permanganates proceeded more efficiently at nickel electrodes than at iron anodes, as suggested by Askenasy,[4] in spite of the lower oxygen over-potential of the former metal. According to these investigators, the mechanism of the oxidation is more complicated than a simple process of ionic transfer :

$$MnO_4'' \rightleftarrows MnO_4' + \oplus$$

and it appears that the presence of oxygen or a superoxide as a catalytic agent is essential for a high electrical efficiency. Müller and Soller[5] observed the specific catalytic agent of lead peroxide anodes in the oxidation of chromates to bichromates, $Cr^{\cdots} \rightarrow CrO_4''$, a marked selective depolarising action of chromate solutions being obtained at the former electrode,

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[1] See Müller and Friedberger, *Zeitsch. Elektrochem.*, 1902, **8**, 230.

[2] D.R.P., 117129/1900.

[3] *J. pr. Chem.*, 1910, **82**, 336.

[4] *Zeitsch. Elektrochem.*, 1910, **16**, 170.

[5] *Ibid.*, 1905, **11**, 863.

whilst at the surface of a platinum anode the electrode-electrolytic potential difference was actually raised by the addition of chromates. Lead peroxide anodes, according to Müller,[1] likewise exert a catalytic action in the oxidation of iodates to periodates:

$$IO_3' \rightarrow IO_4'$$

In various processes of electrolytic oxidation in organic chemistry lead peroxide anodes also exert a marked specific influence. Thus, *p*-nitrotoluene can only be oxidised to *p*-nitrocresol at platinum anodes, but with lead peroxide as anode material, in spite of the lower oxygen over-potential, an almost quantitative yield of *p*-nitrobenzoic acid may be obtained.

PASSIVITY

According to Nernst, we may attribute to all metals an electrolytic solution pressure, characteristic of the element. The difference of potential existing between a metal of electrolytic solution pressure, Ep, immersed in a solution of n valent ions of concentration C, is, as we have noted in the case of the hydrogen electrode, derived from a similar formula:

$$E = \frac{RT}{nF} \log \frac{Ep}{C}$$

It follows that when a certain definite anode electrolyte difference of potential is exceeded, solution of the metal should occur and likewise above a critical catholyte-cathode potential difference precipitation of the metallic ions should take place.

We have noticed that both hydrogen and oxygen show exceptions, the magnitude of the excess or over-potential above the theoretical being dependent on the nature of the electrode. It is extremely probable that similar cathodic over-potential phenomena are to be found in the electro-deposition of metallic ions, but the magnitudes of these discrepancies are usually extremely small. In the case of anodic solution of the metals, on the other hand, over-potentials may frequently assume quite

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[1] *Zeitsch. Elektrochem.*, 1904, **10**, 61.

large values, indicating a case of retardation in the anodic process:

$$M + \oplus \rightarrow \dot{M}.$$

The characteristic value of the electrolytic potential of a metal in a solution containing its ions is greatly influenced by the presence of other electrolytes in the solution.

Cases of catalytic acceleration in the reaction $M + \oplus \rightarrow \dot{M}$ are extremely rare, although in the case of the anodic solution of tungsten metal the addition of hydroxylions appears to exert a catalytic activity in this direction.

The investigations of the more common cases of negative catalysis in the reaction $M + \oplus \rightarrow \dot{M}$, resulting in an apparent reduction of the electrolytic solution pressure of the metal or an ennobling or passification of the element in the solution are very extensive. The mechanism, however, by which passivity is brought about has not yet been thoroughly elucidated.

Keir[1] first observed that iron which had been treated with nitric acid lost its property of precipitating metals such as copper or silver from solutions of their salts. Schönbein[2] obtained similar results with iron which had been made the anode in an electrolytic cell. He likewise introduced the term "passivity." In the same year, Faraday[3] advanced the so-called oxide film theory of passivity. Faraday suggested that the passivity of a metal was essentially due to a surface oxidation process in which an invisible film of oxide was formed on the surface by immersion in oxidising solutions or by electrolytic processes.

Later investigations have shown that many other metals exhibit this phenomenon, notably nickel, cobalt, chromium, platinum, tungsten, and molybdenum, whilst nearly all the other metallic elements possess the property to a minor degree.

The work of Haber and Goldschmidt[4] on anodic polarisation in alkaline solution, of Müller and Spitzer[5] on the anodic

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[1] *Phil. Trans.*, 1790, **80**, 359.

[2] *Pogg. Ann.*, 1836, **37**, 340; 1837, **53**, 41; 1838, **43**, 103.

[3] *Phil. Mag.*, 1836, **9**, 53.

[4] *Zeitsch. Elektrochem.*, 1906, **12**, 49.

[5] *Zeitsch. anorg. Chem.*, 1906, **50**, 321. See also Cohen, *Proc. K. Akad. Wetensh. Amst.*, **17**, 680, 1914.

polarisation of oxide films of iron cobalt and nickel, of Krassa[1] on passivity in strong alkalies and of Grube[2] on the electrolytic oxidation of ferrocyanides at metallic anodes, all lend considerable support to Faraday's theory.

On the other hand, Müller and Konigsberger[3] could not detect any difference in the reflecting powers of an active cathode and a passive anode, whilst if an anode film of even molecular dimensions had been present they stated that they would have been able to observe it. Fredenhagen pointed out[4] that the oxide film theory appeared incompatible with the fact that the anodic potential of active and passive metals could assume apparently stable intermediate values; whilst Finkelstein[5] could find no evidence of an oxide film by measurements of condenser capacity. Although all these criticisms have been ably met by the defenders of the oxide film theory, yet the alternative theories of Finkelstein and Le Blanc have both received considerable support.

According to Finkelstein[6] and Krüger[7] the active and passive forms of the element are due to the presence of modifications of different valencies in the electrode. Experimental proof of the existence of these modifications is wanting, although Hittorf[8] noted that active chromium dissolved in the divalent form, whilst passive chromium only went into solution in the hexavalent condition.

Various investigators, on the other hand, have rejected the mechanistic theory of Faraday and the allotropic view advanced by Finkelstein, and have sought an explanation in the effect of catalytic acceleration and retardation of the primary anodic reaction:

$$M + \oplus \rightarrow \dot{M} \rightarrow \dot{M}.nH_2O,$$

a view originally propounded by Le Blanc,[9] who sought a solution in the relative speeds with which the ions were removed from the metal surface by hydration

$$\dot{M} + nH_2O \rightarrow \dot{M}.nH_2O.$$

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[1] *Zeitsch. Elektrochem.*, 1909, **15**, 490.
[2] *Idem.*
[3] *Ibid.*, 1907, **13**, 659.
[4] *Ibid.*, 1909, **15**, 440.
[5] *Ibid.*, 1909, **15**, 490.
[6] *Ibid.*, 1907, **13**, 659.
[7] *Ibid.*, 1904, **10**, 832.
[8] *Zeitsch. physikal. Chem.*, 1900, **34**, 395.
[9] *Ibid.*, 1904, **48**, 577.

Activation of a metal would thus entail an acceleration of the process of hydration.

Sackur[1] rejected Le Blanc's hypothesis of direct catalytic retardation of the primary anodic reaction and suggested that every metal, being in equilibrium with the hydrion in the solution, must of necessity contain some dissolved hydrogen,

$$2M + 2\dot{H} \rightleftarrows 2\dot{M} + H_2,$$

and passivity phenomena were caused by the slowness of the reaction between the dissolved hydrogen and the liberated anion :

$$2H_2 + O_2 \rightarrow 2H_2O.$$

Fredenhagen, Muthmann, and Frauenberger[2] attribute passivity phenomena to the slowness of the reaction between the metal and the discharged anions :

$$4M + O_2 \rightarrow 2M_2O \leftrightarrows 4\dot{M} + 2O''$$

which results in the accumulation of gaseous oxygen in the electrode.

According to Foerster,[3] all normal metals exist in the passive condition and only become active in the presence of a catalyst, whence we obtain a direct stimulation of the primary process of anodic solution :

$$M + \oplus \rightarrow \dot{M}.$$

Evidence is given for assuming that molecular hydrogen is an active catalyst, whilst Grave[4] contends that the hydrogen ion is the primary catalyst in this reaction, since molecular hydrogen does not restore the activity to passive metals.

As a general rule, although intermediary values of the electrode potential between the active and the passive forms can be obtained and appear to be stable, yet actual transition from active to passive form or *vice versa* can frequently be accomplished with great rapidity, *e.g.*, by touching passified metals with active metal. Schönbein, Ostwald, and Fechner

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[1] *Zeitsch. Elektrochem.*, 1908, **14**, 612 ; see also Haber and Zawadzki, *Zeitsch. physikal. Chem.*, 1911, **18**, 228.

[2] *Zeitsch. physikal. Chem.*, 1903, **43**, 1 ; 1908, **63**, 1 ; *Sitzungsber K. Akad. München*, 1904, **36**, 201.

[3] *Abh. d. Bunsen. Gesellschaft*, 1909, 2 ; *Zeitsch. Elektrochem.*, 1916, **22**, 85.

[4] *Zeitsch. physikal. Chem.*, 1911, **71**, 573.

noticed oscillations in both the gas discharge and the electromotive force of a cell formed of an active and a passive strip of the same metal. The periodic character and the influence of certain added electrolytes are strongly reminiscent of Bredig's experiments on the periodic decomposition of hydrogen peroxide at a mercury surface and of the electrical pulsations obtained by Lewis with mercuric cyanide in a capillary electrometer.[1] Ostwald, as has already been noted (p. 391), obtained a similar periodic evolution of hydrogen in the anodic solution of chromium.[2] It must be admitted that both the Sackur and the Fredenhagen-Muthmann hypotheses appear very like the Faraday theory in the guise of ionic nomenclature. Consequently, there remain only three theories of passivity which may be regarded as fundamentally different in idea.

(*a*) The passivity is due to the presence of oxygen in the electrode, as originally suggested by Faraday. The oxygen may be present in solution as an alloy or as a compound; phenomena such as supersaturation accompanied by the sudden evolution of oxygen in the form of a gas film or liberation of an oxide as a separate phase may take place under conditions which induce a high degree of passivity. The oxide or oxygen alloy film appears to be porous to the electrolyte or electrically conducting when formed under conditions inducing a low passivity. This view has received considerable support by recent investigations on the passivity of metals in alcoholic electrolytes.[3]

(*b*) Passivity is caused by the absence of a catalyst or the presence of a negative catalyst in the electrolyte inducing the rapid hydration of the discharged metallic anions:

$$\dot{M} + n(H_2O) \rightarrow \dot{M},nH_2O.$$

A rapid accumulation of non-hydrated ions would thus take place at the electrode surface, resulting in an increased polarisation.

This view, originally suggested by Le Blanc, offers a ready interpretation of the effect of colloidal additive agents and

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[1] *Trans. Farad. Soc.*, 1912, **8**, 220.

[2] *Zeitsch. physikal. Chem.*, 1900, **35**, 33.

[3] Izgaryschev, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1337.

of various alkaloids enhancing the passivity in solution. The presence of oxidising agents is thus not necessary to produce the phenomenon of passivity.

It may be noted that active polyvalent metals always dissolve in the form of the ions of lowest valency, and it may be reasonable to assume that such ions hydrate with a greater speed than those of higher valency; further, since a high degree of passivity produced by the chemical polarisation of the unhydrated ions is associated with the presence of an electrical double layer due to the charges on the ions between the electrode and film of electrolyte in juxtaposition to it, we may postulate that such a double layer may act as a condenser during discharge, thus accounting for the oscillatory nature of the rate of solution of passive elements, as noted by Ostwald. Although capacity measurements to prove the existence of a condenser formed by such a double layer have yielded inconclusive results,[1] it might be cogently urged that the condenser plate in the liquid phase is extremely mobile and easily destroyed, thus precluding any such measurement.

(*c*) Passivity is the normal state of the elements and activation is caused by the presence of a catalyst accelerating the velocity of the reaction:

$$M + \oplus \rightarrow \dot{M}.$$

According to Foerster, molecular hydrogen is such a catalyst, but more recent experiments have shown this view to be untenable. Grave's argument that the hydrogen ion is a specific catalyst for this reaction is open to serious criticism. It gives no explanation for the passifying action of nitric acid or the increased activation in the presence of halides, since the possible influence of the anions is not included in Grave's hypothesis.

Hittorf likewise noted that chromium readily became passive in hydriodic acid and there is no simple relationship between increasing activity and increasing hydrion concentration.

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[1] See Schulze, *Zeitsch. Elektrochem.*, 1912, **18**, 326.

CHAPTER XIII

CATALYSIS BY RADIANT ENERGY

THE increasing study of the influence of the various forms of radiant energy in the promotion of chemical reaction is resulting in the accumulation of a considerable number of processes in which the catalytic phenomena are completely manifest. They may be characterised in general by the transformation of the radiant energy, most frequently from a higher to a lower vibrational frequency, with a simultaneous acceleration of reaction between the initial constituents, to yield the same end-products, which result at a lower rate from the manifestation of the ordinary chemical forces of the system when uninfluenced by radiant energy.

PHOTO-CATALYTIC REACTIONS

Of such catalytic reactions, those induced by light may first be considered. They comprise a most important subdivision of photo-chemical reactions, and from a study of several such photo-catalytic reactions much of the knowledge of photo-chemical phenomena has been derived. It is necessary to make quite clear at the outset the criteria of true photo-catalytic reactions, since, otherwise, considerable confusion may result, light reactions being frequently complex and composite of several separate and distinct processes. Photo-catalytic reactions, in common with all catalytic processes, will yield the same end-products as the reaction unassisted by the catalyst. The photo-catalyst, therefore, accelerates the promotion of the ordinary equilibrium of a reaction. This criterion rules out a number of reactions which on cursory examination might be regarded as photo-catalytic. Thus, the ozonisation of oxygen at the ordinary temperature by ultra-violet light is not a catalytic process. The reaction proceeds away from the chemical equilibrium at the given temperature. The change is effected at the expense of light energy which is converted into chemical energy, an exact relation existing between the light energy absorbed and the chemical energy produced. In the dark also, the ozonised oxygen decomposes again to oxygen, and the original state is quantitatively reached after a finite interval of time. Similarly, the photo-chemical processes occurring in all plant life are frequently and wrongly assumed to be photo-catalytic. Chlorophyll is not a catalyst of the processes of assimilation, since these are in essence the reduction of carbon dioxide (see page 360),

$$xCO_2 + xH_2O + \text{light} \rightarrow C_xH_{2x}O_x + xO_2,$$

and at the ordinary temperature such a reaction is opposed in direction to that brought about by the operation of the ordinary chemical forces. Chlorophyll, therefore, must itself take part in the reaction. Not so, however, with certain other processes. Thus, for example, hydrogen and chlorine combine in the dark to yield hydrogen chloride. If the original system be suitably illuminated, reaction proceeds much more rapidly to the same end-product. It will be shown later that there is frequently an absence of proportionality between the light energy absorbed and the chemical energy produced; that is to say, a small amount of light is capable of bringing to reaction considerable amounts of the initial system.

The hydrogen–chlorine combination.—Historically regarded, the interaction of hydrogen and chlorine is at once the most important of photo-chemical reactions in general and of photo-catalytic reactions in particular. The acceleration of combination of these gases due to light was observed as early as 1801 by Cruikshank.[1] The phenomenon received further investigation from Gay-Lussac and Thenard,[2] and from Dalton,[3] who showed that the reaction could proceed with explosive violence. A quantitative investigation was under-

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[1] *Nicholson's Journal*, 1801, (i), **5**, 202.

[2] 1810.

[3] "New System of Chemical Philosophy," 1811.

taken by Draper[1] and yielded a most important contribution to photo-chemical knowledge. Thus, Draper enunciated, as a result of his investigations, his now well-known Law of Absorption, which may be expressed briefly in the statement that "Only those light rays which are absorbed by a chemical system are photo-chemically active."

He constructed an apparatus for measuring the intensity of the absorbed rays, terming it a Thitonometer, which consisted simply of a U-tube closed at one end and partially filled with a mixture of hydrogen and chlorine obtained by electrolysis of hydrochloric acid, the gases being stored over hydrochloric acid. On illumination, the gases combined to form hydrogen chloride, which dissolved in the containing liquid, the alteration in level of the meniscus giving a measure of the light energy consumed. In the classical researches of Bunsen and Roscoe,[2] on the quantitative value of the hydrogen–chlorine reaction, the apparatus of Draper was improved. The gases were contained in a suitable vessel with parallel plane surfaces, and were stored over water saturated with the gas mixture. Measurement of the contraction occurring on solution of the hydrogen chloride formed by the reaction was made in a horizontal capillary with attached scale, the meniscus being formed by a thread of water. The displacement of the thread of liquid was governed by the intensity of the illumination and the diameter of the capillary tube, so that, by making this latter narrow, a large displacement of the meniscus could be effected by even weak illumination. A diagrammatic representation of a modified form of Bunsen–Roscoe actinometer is given in Fig. 30. It was used by Burgess and Chapman in the researches later to be detailed, and possesses, in addition, a float contrivance for registering small fluctuations over long periods by means of a lever arm operating a pointer on smoked paper.

The results of the Bunsen–Roscoe study may be summarised. It was shown that the ordinary laws of optics were applicable to the light rays absorbed. The reaction occurring was inversely proportional to the square of the distance from the source of illumination. The laws of reflection and the Beer–

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[1] *Phil. Mag.*, 1841, **19**, 195; 1843, **23**, 401; 1845, **27**, 327.

[2] *Pogg. Ann.*, 1855, **96**; 1857, **100**; 1857, **101**; 1859, **108**.

Lambert Law of Absorption were likewise applicable. The existence of an induction-period, first noted by Cruikshank, and during which the gases increased in reactivity to a maximum, was exhaustively studied. Bunsen and Roscoe showed that the sensitivity of the gases to light was extremely small in the early stages of passage through the "actinometer." On continued passage the sensitivity increased to a fairly reproducible maximum attained after three to six days' passage of gas. They showed that it was necessary to remove air as completely as possible, as the presence of oxygen affected the sensitivity of the gas mixture enormously. Thus, the presence of 0·5 per cent. of oxygen lowered the sensitivity in the ratio of 10 to 1. The induction period was shown to depend upon the depth of gas-layer illuminated. Also, it was shown to be shorter if the light intensity was increased. The length of the induction period was governed also by the previous history of the reacting gas mixture, being greatest with fresh gas and short if the gases had been previously illuminated.

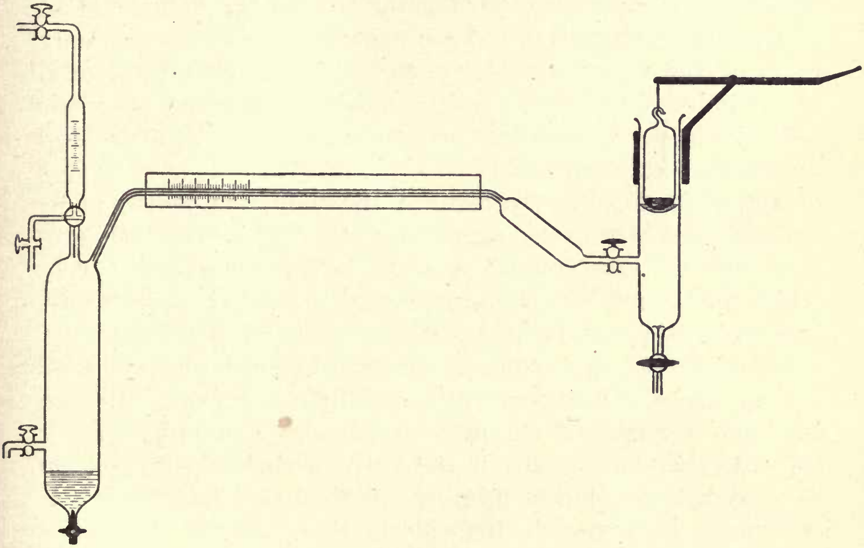

Fig. 30.

The phenomenon of induction has been frequently studied since the work of Bunsen and Roscoe, and has led to a complete explanation. Pringsheim[1] attributed the retarding action of oxygen to the formation of intermediately formed hypochlorous acid, but Mellor[2] showed this to be untenable, since neither Cl_2O nor hypochlorous acid affected the period of induction. The researches of Burgess and Chapman,[3] and of Chapman and Macmahon,[4] established conclusively the real causes of the induction period. These workers showed that the existence of a period of retarded action was always conditioned by the presence of foreign substances already in the containing liquid or on the glass vessels or introduced through the taps. It was not a function of oxygen content of the gas—this only retarded the reaction velocity, but did not affect the length of the induction period. Even oxidising agents such as nitric acid, hydrogen peroxide, or potassium permanganate had no marked influence on the induction. The slightest traces of ammonia, however, prolonged the induction period enormously, and with very small amounts the period was proportional to the amount present. The compounds NCl_3, $NOCl$, ClO_2, and NO_2 similarly retarded reaction enormously, but on the other hand Cl_2O and N_2O were found to be innocuous, pointing to the operation of specific chemical reaction with the hydrogen–chlorine mixture. Similarly, organic nitrogen compounds such as albumen acted like ammonia. It is evident, therefore, that, in the early period of illumination of a hydrogen–chlorine mixture, part of the light energy is consumed in removal, by chlorination, of the impurities present in the reaction vessel, and that the constant maximum reaction velocity represents a state of affairs in which the introduction and removal by chlorination of impurities has reached an equilibrium condition. Obviously, also, if precautions be taken against introduction of impurities and those originally in the containing vessel be removed by illumination of the reaction system, it follows that the induction period would no longer be observed. This was demonstrated by Burgess and Chapman in a simple quartz-glass actinometer, and also by Bodenstein in a series of researches later to be discussed. In the absence of impurities of the types mentioned, the induction period completely disappears.

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[1] *Wied. Ann.*, 1887, **32**, 384.

[2] *J. Chem. Soc.*, 1902, **81**, 1293.

[3] *Ibid.*, 1906, **89**, 1402.

[4] *Loc. cit.*, 1909, **97**, 845.

This explanation of the induction period is not without considerable interest in the general study of catalytic phenomena. The elucidation of the mechanism of induction thus provided should serve as a useful analogy in the discussion of the function of "poisons" in ordinary catalytic operations.

In the investigations of Chapman and his co-workers,[1] as in most of the later work on the hydrogen–chlorine reaction, the technique of Bunsen and Roscoe has been followed. The limitations of the actinometer for purposes of investigation are marked, and with the exception of the work of Chapman and Underhill investigation with the aid of the actinometer has contributed little to the study of the kinetics of the reaction. Bodenstein and Dux, however,[2] by the employment of an ingenious method of measurement of reaction velocity, have contributed materially to the solution of this problem. These workers adapted a method of measurement which eliminated the necessity of employing water as absorbent for the hydrochloric acid formed. Instead, the progress of the reaction under illumination was followed by freezing out with liquid air the residual chlorine and the hydrogen chloride formed during exposure to light, the partial pressure of the unused hydrogen being then measured at temperatures determined by means of an oxygen thermometer. In this manner, the photo-chemical combination of hydrogen and chlorine in varying molecular proportions, and with variable concentrations of oxygen, hydrogen chloride, and water vapour, was exhaustively studied. It was thus established that:

(1) The combination of hydrogen and chlorine under the influence of light is a reaction of the second order, the velocity being proportional to the square of the chlorine concentration. Hydrogen is without influence so long as it is present to the extent of at least one-quarter of the volume of chlorine. At smaller hydrogen concentrations, the velocity decreases slightly.

(2) The hydrochloric acid formed is without influence on the velocity.

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[1] Chapman and Burgess, *loc. cit.*; Chapman and MacMahon, *J. Chem. Soc.*, 1909, **95**, 135, 959; Chapman and Underhill, *ibid.*, 1913, **103**, 496.

[2] *Zeitsch. physikal. Chem.*, 1913, **85**, 297.

(3) Water vapour within certain limits (0·004—2·3 mm.) is also without influence.

(4) Oxygen retards the reaction in such a way that the velocity, at all stages of the combination, is inversely proportional to the concentration of oxygen.

The first of these factors is contrary to an observation of Bunsen and Roscoe, who claimed to have established that an excess of 0·3 per cent. of hydrogen depressed the sensitivity in the ratio of 100 to 37·8. The probable cause of the discrepancy may lie in the presence of oxygen in the Bunsen–Roscoe experiments. The results of Bodenstein and Dux conclusively establish the fact that the concentration of hydrogen, within wide limits, does not affect the reaction.

The absence of any influence of water-vapour within the limits mentioned should be noted. Baker,[1] and later Mellor and Russell,[2] showed that hydrogen and chlorine, when thoroughly dried over phosphorus pentoxide, only slowly reacted in bright sunlight. There is a distinct possibility that by long storage over phosphorus pentoxide chlorine may have reacted with the drying agent and yielded some oxygen, with consequent retardation of the subsequent photo-chemical reaction. The influence of water-vapour on the reaction, therefore, merits more extended investigation. In any case, the results of Bodenstein and Dux are adequate to rule out the theory of reaction mechanism of the hydrogen–chlorine combination suggested by Mellor, who assumes, in explanation, the formation of additive compounds

$$(x\mathrm{Cl}_2,\ y\mathrm{H}_2\mathrm{O},\ z\mathrm{H}_2)$$

as intermediaries in the formation of hydrogen chloride. This explanation has been associated also with the observations of Bevan,[3] of C. T. R. Wilson and of Burgess and Chapman,[4] on the relations between light sensitivity and the formation of fogs in moist hydrogen–chlorine mixtures. Thus Weigert[5] attributes the chemical action of light in such catalytic reactions to the formation of "Reaktionskerne," nuclei of reaction, giving the gas a heterogeneous nature. On such nuclei, the

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[1] *J. Chem. Soc.*, 1894, **65**, 611.

[2] *Ibid.*, 1902, **81**, 1279.

[3] *Proc. Roy. Soc.*, 1903, **72**, 5.

[4] *Loc. cit.*

[5] "Die chemischen des Lichts," F. Enke, Stuttgart, 1912.

concentrations of the reacting gases are increased, causing more rapid reaction according to the law of mass action. The "poisoning" effect of traces of foreign substances is adduced in support of this point of view by analogy with the well-known phenomenon in ordinary heterogeneous catalytic processes. The observations of Bodenstein and Dux on the influence of water vapour must profoundly modify this viewpoint.

For the interpretation of the experimental results of Bodenstein and Dux, the former has developed several interesting theories relative to photo-chemical reaction. It is obvious that the equation of reaction of the hydrogen–chlorine combination may be expressed thus:

$$+\frac{d(2\mathrm{HCl})}{dt} = k\,\frac{J_0(\mathrm{Cl}_2)^2}{(\mathrm{O}_2)},$$

where the quantities in brackets denote concentrations of the respective substances. J_0 denotes the light absorbed, t the time of reaction. Initially, Bodenstein developed an electronic theory of reaction. According to this theory, the initial absorption process in any photo-chemical change is to be regarded as a photo-electric effect, as a rupture of the molecule at the expense of the absorbed light energy into a positive radical—an atom, or, with more complex substances, a molecule with a free valence—and a free electron. Both portions may lead to chemical reaction, the positive radicals in that they are, chemically, exceedingly active; the electrons, in that they may attach themselves to molecules and so activate them as to take part in chemical change. A distinction is drawn between primary light reactions, in which the positive radicals enter into combination, and secondary reactions in which the molecules activated by the electrons take part in the reaction, the electrons, after reaction had occurred, being again free to attach themselves to and activate further molecules. The hydrogen–chlorine reaction would belong to the second of these types, and the reaction would be schematised by the equations:

$$
\begin{aligned}
&(1)\ \mathrm{Cl}_2 + \text{light energy} = \mathrm{Cl}_2 + \ominus,\\
&(2)\ \mathrm{Cl}_2 + \ominus = \mathrm{Cl}_2^-,\\
&(3)\ \mathrm{Cl}_2^- + \mathrm{H}_2 = 2\mathrm{HCl} + \ominus,
\end{aligned}
$$

the negative electron regenerated in (3) being free to undergo the cycle again and again. The retarding influence of oxygen is formulated in this theory by the assumption that the electrons may attach themselves also to oxygen molecules, activate these, yielding probably ozone, which again forms oxygen. Upon such assumptions, Bodenstein shows that the reaction equation experimentally found and given above would also result theoretically, the rate of combination would be proportional to the light energy and to the square of the chlorine concentration, inversely to that of the oxygen and independent of the hydrogen concentration, providing the velocity of (3) were great as compared with that of the others.

According to this viewpoint, the electron would be the catalytic agent of the reaction. A development of the theory as regards the relation of light energy absorbed to chemical reaction produced yields interesting conclusions. In the primary light reactions, in which the positive radicals alone enter into the reaction, it would follow that for every molecule brought into combination a quantum of absorbed energy or a small number of quanta would be necessary. In the secondary reactions, owing to the function of the free electron, as catalyst, an energy quantum should be in a position to bring about the combination of a number of the reacting molecules. Bodenstein calculated that, in his most reactive gas mixture, as many as 10^6 molecules of chlorine were brought into combination with one quantum of light energy. Consequently, any hydrogen chloride formation due to the primary reaction, combination of hydrogen with the positive chlorine rest, is negligible as compared with this extraordinary activity of the secondary reaction. Similar disproportionality between light energy and chemical energy was calculated for other light reactions, which will be later detailed.

Criticism of the electronic theory directed attention to the observations of J. J. Thomson[1] and others that in illuminated chlorine no evidence of ionisation could be obtained. Obviously this criticism might be met on the assumption that recombination of electrons and radical is extremely rapid, so that only by extremely sensitive methods of measurement would ionisation be detected. There is direct evidence that,

[1] "The Conduction of Electricity through Gases."

contrary to the view originally expressed by Draper and subsequently reiterated by several workers,[1] the activity of illuminated chlorine disappears extremely rapidly. Thus Bodenstein and Taylor[2] showed that chlorine would not react with hydrogen, 1/1600th of a second after illumination of the chlorine alone, whereas, if a mixture of both were illuminated, the gases were sufficiently pure for a reaction of explosive violence to occur. The work of Lenard and his pupils[3] forms, however, contributory evidence in opposition to the electronic theory of photo-chemical reaction. These workers show that ionisation, the formation of fogs, and chemical reaction are three quite distinct results of light action which have often nothing to do with each other. Thus fog formation in illuminated chlorine is no evidence of ionisation, and, in the ozonisation of oxygen, ionisation and chemical reaction are affected by different regions of the spectrum and may be separately realised. The later investigations of Le Blanc and Vollmer[4] also show that ionisation is not detectable in hydrogen–chlorine mixture illuminated by an Osram lamp.

Consequently, Bodenstein has been led to a formulation of the hydrogen–chlorine reaction,[5] which does not involve the assumption of electron separation. According to this later theory, the function of the light energy is to bring the chlorine molecules into a rapidly vibrating condition, in which state they may combine with hydrogen to yield hydrogen chloride molecules, themselves possessed of a high energy content transferable to further molecules of chlorine, leading thus to further reaction. The transfer of energy may also take place between hydrogen chloride and oxygen molecules, which latter, therefore, will enter into the kinetic equation as previously outlined. In the development of this viewpoint equations for the kinetics of the equations are deduced similar to those previously derived with the assumption of electron formation, and in agreement with the available experimental

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[1] Favre and Silbermann, *Ann. Chim. phys.*, 1853, (iii), **37**, 497, Cordier and others.

[2] *Zeitsch. Elektrochem.*, 1916, **22**, 202.

[3] *Heidelberger Akad. Ber.*, 1910, Nos. 28, 31, and 32 ; 1911, Nos. 16 and 24 ; Ludlam, *Phil. Mag.*, 1912, (vi), **23**, 757.

[4] *Zeitsch. Elektrochem.*, 1914, **20**, 494.

[5] *Ibid.*, 1916, **22**, 250.

data. The theory forecasts, also, interesting conclusions as to the reaction kinetics in presence of inert constituents, which should prove decisive in any investigation of the correctness of the theory. Obviously, therefore, in spite of the large amount of experimental material which has been accumulated relative to the hydrogen–chlorine combination, further work is necessary for complete elucidation of the mechanism. And the labour involved promises to be rich in reward, since the points at issue have an interest not merely in photochemical catalysis in particular, but also in the problem of catalysis in general, since many of the observations recorded, relative to this reaction, have their analogues in ordinary catalytic processes.

Further photo-catalytic halogenations.—The accelerating action of light is demonstrable in many other processes of halogenation. Thus, the combination of carbon monoxide, of sulphur dioxide, of saturated, unsaturated, and aromatic hydrocarbons, of organic acids, such as acetic acid, with chlorine and the other halogens, may all be stimulated by illumination, and the study of such actions has increased the material at the disposal of the theoretical investigator as well as having contributed to possible technical development.

The photo-catalytic combination of carbon monoxide and chlorine was first observed by Davy[1] and studied quantitatively by Dyson and Harden,[2] by Wilderman,[3] by Weigert,[4] and by Chapman and Gee.[5] The reaction is much less sensitive to light than the hydrogen–chlorine combination, strong illumination causing but weak reaction. Oxygen also inhibits the reaction, and, as was shown by Chapman and Gee, in a remarkable way. The first additions of oxygen have a strongly inhibitive effect, which decreases with further additions, so that with half an atmosphere of oxygen the reaction is but little slower than in presence of one-quarter of an atmosphere. The sensitivity, S, could be expressed by an equation :

$$S = A + \frac{B}{[O_2]},$$

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[1] *Phil. Trans.*, 1812, **144**.

[2] *J. Chem. Soc.*, 1903, **83**, 201.

[3] *Phil. Trans.*, 1902, **199**, (*A*), 337.

[4] *Ann. Physik*, 1907, **24**, 55.

[5] *J. Chem. Soc.*, 1911, **99**, 1726.

where A and B are constants, $[O_2]$ the oxygen concentration. Wildermann concludes from a small series of measurements that the reaction is the usual one of the second order :

$$\frac{dx}{dt} = k[Cl_2][CO].$$

Bodenstein has discussed these results from the point of view of his electronic theory, and shows that the deviations from the hydrogen chlorine reaction are to be sought in the relative non-reactivity of the carbon monoxide with the activated chlorine. He calculates that in the carefully prepared mixture of gases employed by Wildermann 100 molecules of chlorine react per light quantum. Moreover, he observes that, by increase of oxygen concentration, it should be possible almost completely to suppress the secondary reaction which leads to the disproportionality between light energy and chemical energy observed in the hydrogen chlorine reaction, and thereby to emphasise the primary reaction in which proportionality exists. An investigation of such points of interest is promised.

By a study of the phosgene equilibrium in illuminated systems at temperatures of 400–500°, Weigert established the important fact for catalytic reactions that both formation and decomposition of phosgene were catalytically accelerated and that the equilibrium (60–70 per cent. decomposition) was unchanged. Obviously, in this case the dissociation of phosgene is a reaction accelerated by the presence of chlorine, which absorbs the light energy and acts, therefore, as an optical sensitiser of a gas reaction, similar to that well known in the case of photographic plates, where, by impregnation with dyestuffs, the sensitivity of the emulsion for certain spectral regions is increased. Weigert further showed[1] that in the combination of hydrogen and oxygen to form water, in the oxidation of sulphur dioxide to trioxide, and in the decomposition of ozone these reactions could be made sensitive to light, outside the ultra-violet region, by addition of chlorine. Thus, in the de-ozonisation of oxygen in presence of varying amounts of chlorine (6–70 per cent.), employing a mercury-vapour lamp and glass vessels to exclude ultra-violet light,

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[1] *Ann. Physik*, 1907, **24**, 252.

the velocity of reaction was independent of the ozone concentration and determined by the light absorbed by the chlorine only. Weigert cites this as a typical photo-catalytic process, in which a substance is formed by illumination of the chlorine, which practically instantaneously reacts with the ozone to form oxygen.

The photo-catalytic halogenation of the hydrocarbons has been most exhaustively studied in reference to the aromatic hydrocarbons. Luther and Goldberg[1] observed, in the chlorination of benzene, toluene, and xylene, strong inhibition of the catalytic process due to oxygen. Bruner and Czernecki[2] have shown that bromination is also sensitive to oxygen, and leads to quite indefinite rates of reaction unless the oxygen is removed. Addition of iodine to the system in determined amounts effects the removal of oxygen, by reaction to yield oxy-iodine compounds. In absence of oxygen, bromination occurs in the side-chain at a velocity proportional to the intensity of the light I_0 and the concentration of hydrocarbon present, thus :

$$\frac{dx}{dt} = kI_0(\mathrm{C_7H_8}).$$

That the bromine concentration was without influence, was shown by the authors to be due to the experimental arrangements, in which absorption of the light was practically complete even in moderate concentrations. For a homogeneous field of illumination, in other words, with weak absorption, the reaction velocity equation would be

$$\frac{dx}{dt} = kI_0(\mathrm{Br_2})(\mathrm{C_7H_8}).$$

The yield of reaction per quantum of energy absorbed is high when oxygen has been displaced from the system. According to Bodenstein, this can be estimated at 10^6 molecules re-acting per quantum of energy absorbed.

The temperature coefficient of the photo-chemical reaction between bromine and toluene is also of interest. Normally, photo-chemical reactions possess a very small temperature-

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[1] *Zeitsch. physikal. Chem.*, 1906, **56**, 43.

[2] *Bull. Acad. Sci. Cracow*, (*A*), 1910, 576.

coefficient. Thus, Bunsen and Roscoe determined the coefficient for hydrogen–chlorine combination as 1·2 per 10°, whilst later measurements of Roscoe and Denison gave unity. In other words, elevation of temperature normally promotes but little the velocity of a photo-chemical reaction. In the photo-bromination of toluene, however, the temperature-coefficient possesses the relatively high value of 1·85. The corresponding reaction in the dark likewise possesses the high temperature-coefficient of 4, as opposed to the normal value of 2–3. Bodenstein interprets this on the assumption that both bromine and toluene must be active in order to react upon collision (or, interpreted in the recent phraseology of energetics, both molecules must receive a definite critical increment of energy before reaction occurs).[1] In the light reaction, the temperature-coefficient 1·85 represents the increase, for temperature rise of 10°, of active molecules of toluene, whilst $4·0/1·8 = 2·2$ represents the increase in active bromine molecules. In this manner, it is suggested, an increase in our knowledge of ordinary chemical processes may result from a study of photo-chemical reactions.

Photo-catalytic oxidation.—In agreement with the Draper Law of Absorption, photo-chemical halogenation occurs in presence of light from the visible portion of the spectrum. Chlorination is promoted principally by the blue and violet light rays. Many other reactions, however, are catalytically accelerated by the ultra-violet regions of the spectrum, and among such may be included a number of photo-catalytic oxidation processes. Of oxidation processes in gaseous systems, attention may be directed to the photo-chemical acceleration of the oxidation of sulphur dioxide to sulphur trioxide, of hydrogen to water vapour, and of carbon monoxide to carbon dioxide. All these processes have been studied under the influence of the light from the electric arc or the mercury vapour lamp.

From the point of view of reaction kinetics, little has resulted, as yet, from such investigations, in large measure owing, doubtless, to the difficulties of experimental technique. The evidence points to the action of a catalytic agent resulting from the action of light on the oxygen. In the investigation

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[1] See Lewis, *J. Chem. Soc.*, **105**, 1914 *et seq.*

of the oxidation of sulphur dioxide by Coehn and Becker[1] the main feature of the results obtained is the photo-chemical equilibrium set up. It was found that, with the gases in stoichiometric proportions, the equilibrium attained, over a temperature range of 50° to 800°, was constant and corresponded with an SO_3 content of 65 per cent. With variation of the concentrations of the reacting substances, varying equilibria were obtained corresponding with those demanded by the law of mass-action. The precise explanation of this feature is still wanting, and awaits, doubtless, the formulation of the reaction mechanism.

The combination of hydrogen and oxygen under the influence of ultra-violet light, studied by Andreew,[2] was shown to be a reaction independent of the concentration of the reacting gases. Coehn and Grote,[3] on the other hand, claim that it is a reaction of the first order. In reality there is, probably, no discrepancy between these two results, since Andreew worked with a mixture of the two gases alone, whilst the observations of Coehn and Grote were carried out with the minimal quantities of the two gases present near the equilibrium state of the system. The order of reaction is governed by the degree of absorption of the active rays, and, in the simple hydrogen–oxygen mixture, if this were complete, a reaction of the zero order would result in which the reaction velocity is independent of the concentrations of the reacting substances.

Definite information as to the function of the various substances present in such oxidation processes emerges from the interesting research of Chapman, Chadwick, and Ramsbottom[4] on the oxidation of carbon monoxide. It was definitely shown in this work that ozone was simultaneously produced, and that, moreover, carbon monoxide acted as an inhibitor of ozone decomposition. For, whereas under the experimental conditions employed, pure dry oxygen yielded only 3·5 per cent. of ozone, it was found that, when dry carbon monoxide was present, the ozone concentration rose to as much as 19 per cent. with simultaneous formation of but 10 per cent.

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[1] *Zeitsch. physikal. Chem.*, 1910, **70**, 88.

[2] *J. Russ. Phys. Chem. Ges.*, 1911, **43**, 1342.

[3] "Nernst Festschrift," Halle, 1912, p. 136.

[4] *J. Chem. Soc.*, 1907, **91**, 942.

of carbon dioxide. Further, it was shown that water acted either as an accelerator of ozone decomposition or as a promoter of the oxidation of carbon monoxide ; for, if the gases were saturated with water vapour at the ordinary temperature only one per cent. of ozone was produced with the same illumination as that cited in the case of the dry gases, whilst, simultaneously, as much as 28 per cent. of carbon dioxide was produced.

Of oxidation processes in liquid system the oxidation of hydriodic acid may be cited. Since this reaction has been employed for actinometric purposes, it has been frequently studied and most thoroughly by Plotnikow.[1] The process is, in reality, the oxidation of the iodide ion in acid solution by atmospheric oxygen, a reaction which, as is well known, takes place slowly in the dark, much more rapidly, however, when illuminated. Plotnikow showed that the photo-chemically active rays (the blue and violet of the mercury arc) were but feebly absorbed by the reacting system. Obviously, therefore, the reaction must be exceedingly light-sensitive, which fact also emerges from a computation of Bodenstein that 10^{10} molecules of oxygen react per quantum of light energy absorbed. The now familiar influence of impurities or added substances on the velocity of reaction is in this case also marked. The nature and concentration of the acid employed determine the reaction velocity. Certain added substances, as, for example, quinine, accelerate the reaction largely ; others act inhibitively. Bodenstein has suggested an interpretation of the experimental results, assuming activation of oxygen by electrons set free from the hydriodic acid or accelerators present in the system. Weigert suggests the mechanism of reaction nuclei on which the oxygen is condensed at a higher reacting potential. He points to the proved existence of peroxide compounds in several of the investigated cases of photo-chemical oxidation. Thus, Richardson[2] was able to demonstrate the presence of hydrogen peroxide in the photo-chemical oxidation of oxalic acid, ether, and amyl alcohol.

The promotion of peroxide formation by photo-catalytic means has attained technical importance in connection with

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[1] *Zeitsch. physikal. Chem.*, 1907, **58**, 214.

[2] *Ibid.*, 1894, **15**, 505 ; 1897, **22**, 650.

a series of reactions elsewhere discussed in the section on autoxidation. The production of rapid-drying oils by preliminary exposure to light is now a recognised technical process. Illumination evidently promotes the formation of autocatalysts, presumably of the peroxide type, which subsequently accelerate the oxidation and drying of the oil on exposure to air.[1]

The presence of hydrogen peroxide has also been demonstrated by Weigert[2] in the solutions obtained after the photocatalytic oxidation of quinine by means of atmospheric oxygen. This reaction is remarkable in other ways, since, as is obvious from the experimental results obtained, oxygen, although participating in the reaction, also acts as an inhibitor. The product of the reaction velocity and the oxygen concentration was shown to be constant over a considerable range. With complete absorption of light, the velocity of action is proportional to the quinine concentration. The reaction is likewise sensitive to foreign additions. Thus, in presence of 0·1 normal sulphuric acid, reaction is completely suppressed.

The oxidation of quinine with chromic acid as oxidising agent was studied in detail by Luther and Forbes.[3] In this case, the reaction velocity is determined by the light absorbed by the molecules of quinine. The chromic acid is not the light-sensitive agent. The reaction is not markedly sensitive to impurities, and occurs quite rapidly in high acid concentrations, in marked contrast to the previous case of oxidation by atmospheric oxygen. Luther and Forbes, by a study of the reaction under the influence of varying wavelengths, were able to demonstrate elegantly the influence of absorption on the order of reaction. The violet region of the mercury vapour lamp is only feebly absorbed by quinine. In this region the reaction is monomolecular. At the ultraviolet end of the spectrum the absorption was practically complete and the reaction in that region was of zero order. Only at low concentrations has the chromic acid any influence on the reaction velocity, which points, obviously, to the

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[1] See, in this connection, p 149, and Fahrion, *Chem. Zentr.* 1905, **1**, 305; Genthe, *Zeitsch. angew. Chem.*, 1906, **19**, 2087; 1909, **22**, 2095.

[2] "Nernst Festschrift," Halle, 1912, p. 464.

[3] *J. Amer. Chem. Soc.*, 1909, **31**, 770.

conclusion that, by interaction of light and quinine, a photo-catalyst results which then reacts with the chromic acid. As is usual with successive reactions of this type, the *tempo* of the whole process is governed by the slowest of the individual reactions, and this in turn is determined by the concentrations of the reacting substances.

Photo-catalytic oxidation in presence of chromates as oxidising agents has found extended technical application in photographic and lithographic processes. The application is based on the discovery that substances such as gelatin, glue, fish-glue, albumen, etc., when heated with solutions of chromates, are rendered partially or completely insoluble in water after exposure to light. The degree of insolubility is proportional to the intensity of illumination. In photography, using pigmented gelatin layers, this has led to the beautiful "carbon process" and numerous allied processes. In lithography employing metallic bases covered with a chromated gelatin layer or layers of similar substances, the permeability to acids is determined by the intensity of illumination. Thus it is possible to obtain etched reliefs from which, by the ordinary printing processes, prints may be obtained. The actual mechanism of the photo-chemical action on the colloidal material, although the object of considerable investigation, is, as yet, not satisfactorily settled. In its main features it is undoubtedly parallel to the case of quinine just discussed. But the mechanism whereby insolubility is produced is not yet clear.

A photo-catalytic process of common everyday observation is the fading of coloured materials and pigments on exposure to light. Whilst possibly not exclusively oxidation processes, it has been shown in many cases that the reactions are autoxidations catalytically accelerated by light. Weigert[1] has shown, for example, that with substances like fluorescein and erythrosin, the mechanism is parallel to that observed by him for quinine. Lasareff has, however, demonstrated[2] that, in thin colloidal films, the bleaching of pigments is due, not only to oxidation, but also to intramolecular decomposition. Also the complexity of the problem is intensified by the influence of added substances. Thus, it has been demonstrated,

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[1] *Loc. cit.*

[2] *Zeitsch. physikal. Chem.*, 1912, **78**, 657.

by observations with the ultramicroscope,[1] that addition of potassium ferrocyanide gives rise to a heterogeneous catalyst, peroxidic in nature. The addition of iodine strongly accelerates certain of these reactions, as does also the presence of the ions OH', NO_3', ClO_4'. Retardation occurs in presence of $H^{\cdot}$, Cl', Br' and SO_4' ions.

The formation of an autocatalyst, of which the activity persists for long periods after illumination has been discontinued, is well illustrated in the case of the oxidation of iodoform.[2] On bubbling oxygen through illuminated solutions of iodoform in the most diverse solvents, oxidation occurs, with separation of iodine. The velocity of reaction increases with increasing initial concentration of iodoform in degree corresponding with that required in accordance with Beer's Law. The velocity varies with the nature of the solvent. Thus, in carbon tetrachloride solution, the reaction is fourteen times as rapid as in alcohol. The influence of iodine is, however, most marked. For, although in the replacement of iodoform by iodine during the course of the reaction the absorption of light is strongly altered, still the velocity of reaction remains constant. Also, after discontinuance of illumination, the process of oxidation continues steadily for long periods in the dark. If, also, to an unilluminated solution of iodoform in certain solvents a small amount of a pre-illuminated solution be added, oxidation takes place without any further illumination. Obviously, illumination gives rise to a photo-catalyst which persists in activity over long intervals. The phenomenon is not definitely explained. The process is undoubtedly complex and presumably is quite different in different solvents, since only in certain solvents is the activity, on discontinuance of illumination, observable.

Photo-catalytic hydrolysis.—The hydrolysis of hydrochloroplatinic acid has been shown by Boll and Jacob[3] to be photo-chemically sensitive to ultra-violet radiation. The different acids H_2PtCl_6, $H_2PtCl_5(OH)$, $H_2PtCl_4(OH)_2$, and

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[1] See Amanns, *J. Suisse de Chem. et pharm.*, 1901 ; Kistiakowski, *Zeitsch. physikal. Chem.*, 1900, **35**, 431.

[2] Szilard, *Zeitsch. wiss. Photochem.*, 1904, **4**, 127 ; Plotnikow, *Zeitsch. physikal. Chem.*, 1910, **75**, 337, 385.

[3] *Compt. rend.*, 1912, **154**, 881 ; 1912, **155**, 826 ; 1913, **156**, 138, 691.

$H_2PtCl_4(OH)_2$ are all hydrolysed by water, the rate of reaction being readily followed with great exactitude by determination of the conductivity of the solution. The formation of hydrochloric acid during the reaction causes an increase of conductivity. With weak absorption, the reaction is of the second order; with considerable absorption, the velocity is proportional to the chloroplatinic acid concentration. The authors regard this reaction as pointing to the formation of a compound, $H_2PtCl(OH)_5 \cdot H_2Pt(OH)_2$, the production of which is suggested also by a measure of the absolute amount of hydrochloric acid produced. By direct measurement it was shown that, in 1/10000 normal solution, about two molecules of acid were decomposed per quantum of light energy absorbed. In stronger solutions, the number decomposed would probably be proportionately greater. By analogy with the hydrogen–chlorine reaction, Bodenstein suggested that the reaction should be inhibited by oxygen. Boll and Henri, however,[1] on submitting this point to experimental test, could not confirm this suggestion, and consequently doubt was cast on the whole systematisation introduced by Bodenstein.

From the quantitative point of view, the mechanism of numerous photo-chemical reactions has been studied by Henri and his co-workers. Of the reactions included under hydrolysis, that of acetone may be cited. Henri and Wurmser[2] showed that the reaction was photo-chemically quite sensitive, the ratio of molecules hydrolysed to quanta absorbed being in the ratio of 200 to 1. Baly[3] suggests, however, in regard to this result, that a portion of the necessary energy for the reaction is derived from the solvent, which exerts, according to this view, an influence in opening up the electrical fields of force of the solute molecules. Of interest also from the same work of Henri and Wurmser is the observation that the minimum of energy capable of producing luminous sensation in the eye is inferior to the elementary quantum of energy.

Photo-catalytic decomposition and polymerisation.—Typical examples of decomposition photo-chemically acceler-

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[1] *Compt. rend.*, 1914, **158**, 32.

[2] *Ibid.*, 1913, **156**, 1012.

[3] *Physikal. Zeitsch.*, 1913, **14**, 893.

ated are the decomposition of ozone and hydrogen peroxide, together with the decomposition of oxalic acid in presence of uranyl salts. All three reactions have been the object of a considerable amount of experimental work, from which certain conclusions relative to the reactions may be drawn.

Thus, in the decomposition of ozone it was shown by Regener[1] that ultra-violet light in the region of $0{\cdot}257\mu$ was particularly active. The kinetics of the reaction has been studied, more especially by von Bahr[2] and by Weigert.[3] With complete absorption of light, reaction is proportional to the ozone concentration. With homogeneous illumination, that is, with extremely thin gas layers, the reaction would be proportional to the square of the ozone concentration, which is in part made manifest in the available experimental data. From Weigert's data, it may be calculated that, in his experiments, approximately 100 molecules of ozone are decomposed per quantum of energy absorbed. In an investigation on the activation of oxygen by illumination, Weigert determined the influence of hydrogen in the decomposition of ozonised oxygen. With small concentrations of ozone and excess of hydrogen, water is practically exclusively formed, but, in the reverse case, with low hydrogen concentrations, oxygen is the product of decomposition. Bodenstein interprets these results as showing that oxygen inhibits the reaction, the hydrogen acting in the main as diluent for the oxygen inhibitor. He points out further that the yield of chemical energy per energy quantum absorbed is increased tenfold by addition of hydrogen.

In connection with the decomposition of hydrogen peroxide under illumination it was demonstrated by Kistiakowski[4] that by addition of red and yellow prussiate of potash the catalytic action of light was prolonged for considerable periods after illumination had ceased. Ultramicroscopic investigations showed that this could probably be attributed to formation of a heterogeneous catalyst. More recently, it has been shown that other substances may act in the reverse direction. Thus, Henri and Wurmser[5] have shown that traces of numerous substances, and especially of alkalis, render hydrogen peroxide

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[1] *Ann. Physik*, 1906, (iv), **20**, 1033.

[2] *Ibid.*, 1910, (iv), **33**, 598.

[3] *Zeitsch. physikal. Chem.*, 1912, **80**, 78.

[4] *Ibid.*, 1901, **35**, 431.

[5] *Compt. rend.*, 1913, **157**, 284.

solutions stable to ultra-violet light. As to the kinetics of the decomposition, Tian[1] reports that in dilute solution the reaction is of the first order. More recently, however,[2] he published figures which point to the fact that the decomposition is proportional to the light absorbed and the concentration of peroxide, and that the oxygen evolved in the reaction acts as an autocatalytic inhibitor. Henri and Wurmser[3] report but feeble absorption of the light energy and a decomposition of more than 100 molecules per quantum absorbed.

The decomposition of oxalic acid in presence of uranyl nitrate is very sensitive to light. Between the concentration limits of $N/1000$ and $N/10,000$ the velocity is strictly proportional to the absorbed energy,[4] and 500 molecules of acid are decomposed per quantum of energy absorbed. The hypothesis of Bodenstein that oxygen would act as inhibitor of this reaction was also shown by Henri and Boll[5] to be in disagreement with experimental facts.

The photo-chemical acceleration of processes of polymerisation may be exemplified in the researches of Berthelot and Gaudechon[6] on acetaldehyde. In presence of moisture and oxygen, acetaldehyde is rapidly oxidised by ultra-violet light to acetic acid. Even in absence of oxygen, with the extreme rays of ultra-violet light, oxidation sets in, presumably with simultaneous decomposition. In absence of moisture, and most rapidly in the vapour phase, acetaldehyde resinifies and forms polymerised products on illumination with rays of wave-length less than $0{\cdot}25\mu$.

CATALYSIS BY MEANS OF RÖNTGEN RAYS, THE SILENT DISCHARGE, AND RADIOACTIVE SUBSTANCES

In the preceding sections of this chapter it has emerged that light energy may promote widely diverse and distinct catalytic reactions. In most cases from lack of full investigation it has been impossible to determine the actual *modus*

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[1] *Compt rend.*, 1910, **151**, 1040.

[2] *Ibid.*, 1913, **156**, 1879.

[3] *Ibid.*, 1012.

[4] Boll, *ibid.*, 1913, **156**, 1891.

[5] *Ibid.*, 1914, **158**, 32.

[6] *Ibid.*, 1913, **156**, 233.

operandi, but it is obvious that in many cases the function of the light energy absorbed has been the production of a catalytic agent which has accelerated the operation of a reaction in the normal direction of the chemical forces. It would be expected, therefore, that in the operation of other forms of radiant energy on chemical systems similar catalytic effects would be observed. Thus, an examination of the material available concerning the influence of the silent electric discharge, of Röntgen rays, and of the radiations emitted during radioactive transformations should reveal examples parallel to those cited in the sections dealing with photo-chemical changes.

The literature of chemical reactions induced by these different types of radiation is scanty, however, doubtless due to the recent date of their discovery and elucidation. In the main, the literature deals with reactions which cannot be included in the scope of this study, since they are chiefly non-catalytic and in which the reaction occurring is in the direction opposed to the normal chemical forces of the system, deriving the necessary energy from the radiant energy supplied. Thus, in the case of the silent electric discharge the formation of ozone from oxygen is an excellent example. As Kruger has recently shown,[1] the number of ozone molecules formed is determined by the number of oxygen molecules which are ruptured by the electrons introduced into the gas system.

The decomposition of dry ammonia gas under the influence of the silent discharge is another case parallel to the ozonisation of oxygen. Curiously, however, as was shown by Le Blanc and Davies,[2] addition of nitrogen to the ammonia accelerates the decomposition considerably, whereas hydrogen diminishes reaction. These influences are worthy of more extended investigation.

The researches of Fassbender[3] demonstrated the catalytic influence of the silent discharge in the combination of carbon monoxide and oxygen and of hydrogen and chlorine. The alternating field required is much more powerful in the former case, as would be anticipated from the photo-chemical results.

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[1] "Nernst Festschrift," Halle, 1912.

[2] *Zeitsch. Elektrochem.*, 1908, **14**, 361.

[3] *Zeitsch. physikal. Chem.*, 1908, **62**, 743.

Doubtless, investigation of the latter case would show that as regards kinetics and energy consumption it was parallel to that observed under the influence of light, Röntgen rays and alpha-particles, which latter will subsequently be detailed.

The function of Röntgen rays in promoting a reaction catalytically is best exemplified in the case of the hydrogen–chlorine combination as studied by Le Blanc and Vollmer.[1] It was found that in a hydrogen–chlorine mixture which was photo-chemically quite sensitive, Röntgen rays also produced combination. Moreover, in evaluating the ratio of energy supplied to the amount of chemical combination produced, it was shown that 10^4 molecules of chlorine combined for each electron produced in the system by the radiation. The kinetics of the reaction was not studied and remains therefore an interesting problem for comparison with the effect of light energy and of the action of alpha-particles on the same reaction.

A number of qualitative tests on certain reactions, as, for example, the hydrolysis of acetone, catalytically accelerated by light, have been made, by one of the authors, with Röntgen rays from a Coolidge tube, but without significant result. That a search for such reactions need not be fruitless, however, is to be concluded from the recent observations of Bordier[2] on the decolorisation of aqueous solutions of iodine and of starch iodide by exposure to Röntgen rays for a few minutes. The quantity of radiation required varied with the proportion of iodine in the solution. Further investigation would doubtless reveal the high catalytic activity of the rays in this particular reaction, and data on the energy quantities involved should be interesting.

Van't Hoff[3] forecasted the possibility of using radioactive transformations and the energy resulting therefrom as catalytic agents. In evidence of his belief, he directed attention to the action of radioactive materials on the glass vessels in which they were contained. Especially with glasses containing manganese or lead, the coloration produced in the glass by action of the rays evidences an acceleration of a reaction, presumably oxidation, which ordinarily takes

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[1] *Zeitsch. Elektrochem.*, 1914, **20**, 494.

[2] *Compt. rend.*, 1916, **163**, 291.

[3] *Zeitsch. Elektrochem.*, 1903, 9, 736.

place but slowly, being manifested in glass of manganese content by the development of a pinkish tinge.

The reactions brought about by radiations from radioactive substances have been collected and discussed by Lind.[1] The reactions investigated are numerous and include, among others, the formation and decomposition of water, of ammonia, of hydrogen chloride and bromide, the decomposition of carbon monoxide and dioxide, and the ozonisation of oxygen. From a review of the available material Lind was able to establish a definite relationship between the number of molecules brought to reaction and the pairs of ions formed, for example, by the alpha-particles introduced into the system. Thus, in the case of ozonisation of oxygen, most carefully and thoroughly investigated by Lind, it was shown that for every pair of ions, one molecule was caused to react. The reactions may therefore be regarded as due to the direct intervention of the alpha-particles the energy from which is transformed in the process of the chemical reaction.

The conspicuous exception to the simple relation thus formulated by Lind for the reactions brought about by radioactive energy is again to be found in the case of the hydrogen–chlorine combination. Lind calculated, from experiments of Jorissen and Ringer,[2] that, from one pair of ions, the number of chlorine molecules brought into reaction was of the order 10^2-10^3, similar in magnitude to that observed by Le Blanc and Vollmer for the action of Röntgen rays, and paralleled also by the previously cited computations for the photochemical reaction. The experiments of Jorissen and Ringer were carried out with the gases in an actinometer having a suitable scale attachment, radium salt being contained in a thin-walled tube fitted into the reaction vessel. Evidence for an induction period is manifest from the experimental results as well as for a varying sensitivity of the reacting gases, due, doubtless, to impurities present in the gases.

The analogy between the photo-chemical reaction and that induced by the alpha-particles is still further emphasised by a study of the kinetics of the reaction.[3] The experimental conditions were so arranged that complete absorption of the

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[1] *J. Physical Chem.*, 1912, **16**, 564.

[2] *Ber. Chem. Ges.*, 1906, **39**, 2065.

[3] Taylor, *J. Amer. Chem. Soc.*, 1914, **37**, 24; 1916, **38**, 280.

alpha-particles from radium emanation in a minute, thin-walled glass bulb was effected in the hydrogen–chlorine mixture surrounding the bulb and contained in a spherical reaction vessel of radius greater than the range of the alpha particles (Fig. 31). In these circumstances of complete energy absorption, it was shown that the reaction velocity was proportional to the energy absorbed and was of the first order, inversely proportional, however, to the total pressure which changed during an experiment by withdrawal of samples for analysis. These results could be interpreted by a reaction equation of the form:

$$\frac{d2\text{HCl}}{dt} = R\frac{E_{\text{abs}} \times [\text{Cl}_2]}{[\text{O}_2]},$$

which, for small energy absorption such as holds in the photo-chemical reaction, would change to the square of the chlorine concentration and yield therefore a reaction equation identical with that obtained by Bodenstein and Dux in the photo-chemical reaction. On the energy side, it was computed that, with the most reactive gas mixture employed — which, however, was considerably less sensitive, photo-chemically, than the gases of Bodenstein and Dux—as many as 2×10^4 molecules of chlorine reacted for every pair of ions introduced into the reaction space, thus

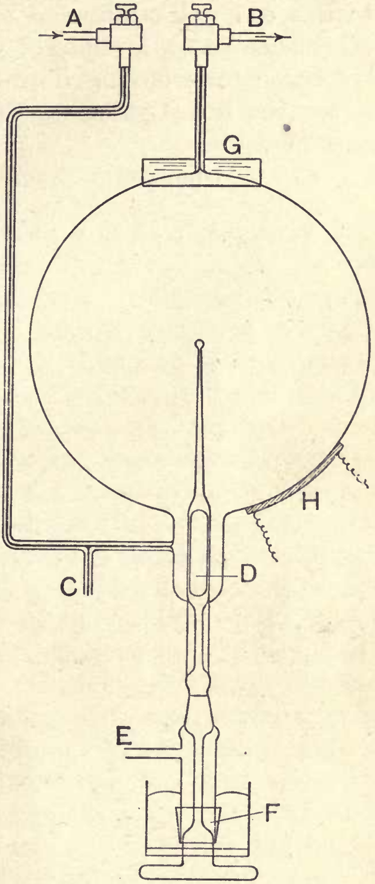

Fig. 31.—*A*, Gas inlet; *B*, gas outlet; *C*, manometer connection; *D*, silica rod as compensator for thermal expansion of mercury; *E*, inlet for emanation; *F*, mercury scale; *G*, ice reservoir, *H*, electric heater, to ensure rotation of gases.

confirming the calculation of Lind relative to Jorissen and Ringer's work and establishing conclusively the catalytic influence of the alpha particles in the reaction.

Thus far, the catalytic action of alpha-particles is restricted to this one well-established case. Doubtless there are many other such cases, a study of which, and of the corresponding behaviour towards other forms of radiant energy, would richly repay the investigator in the search for the mechanism of such changes.

CHAPTER XIV

CATALYSIS IN ANALYTICAL CHEMISTRY

THE recognition of the applicability of catalytic operations to the purposes of analytical chemistry dates from the earliest days of the investigation of catalysis. Döbereiner's experiments on the combustibility of oxygen–hydrogen mixtures in presence of platinum wire and Sir Humphry Davy's parallel researches on the ignition of coal gas–oxygen mixtures by means of fine platinum wires introduced into them at a temperature below the ignition point were both of especial and recognisable significance in the problem of the analysis of gaseous mixtures. Indeed, already in 1824, Turner, in a communication to the Royal Society of Edinburgh, published in the Edinburgh *Philosophical Journal*,[1] had discussed the experiments of Döbereiner and of the possible extension of his method to the promotion of combination between other gases such as hydrogen and chlorine or iodine. Turner, moreover, envisaged the possibility of a separation of gases by means of fractional combustion, but was unsuccessful in his attempts. Immediately afterwards, the studies of W. Henry[2] demonstrated the use of platinum in fractional combustion in a series of researches still of remarkable and fundamental import to the student of catalytic processes.

In a similar manner, the catalytic reactions were exploited in the direction of analytical application, either qualitative or quantitative. The discovery of the efficacy of platinum as oxygen carrier found manifold developments. Thus Döbereiner's demonstration of the oxidation of alcohol to acetic acid in presence of platinum or iridium sponge[3] was later

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[1] 1824, **11**, 99, 311.

[2] *Phil. Mag.*, 1825, **65**, 269.

[3] *Schweigger's J.*, 1831, (iii), **63**, 476.

applied as test for alcohol.[1] Rose,[2] recognising the accelerating action of platinum on the combustion of organic substances, recommends the addition of platinum black in the determination of ash in combustible matter, the principle being later extended to other contact substances, for example, ferric oxide[3] and silver.[4] Copper and its compounds were early recognised for their catalytic properties, and found application in analytical operations, chiefly in gas analysis, organic analysis, and as accelerators for solution processes. Thus, Williams utilised the copper–zinc couple[5] for reduction and estimation of nitrates. The siccative action of metallic lead, discovered by Chevreul,[6] was the forerunner of the numerous analytical methods for the determination of the oxidation of drying oils. The decomposition of hydrogen peroxides by finely divided platinum metals, another of the catalytic reactions already known in the Berzelius period of activity in matters catalytic, was also applied later to the gas volumetric determination of the peroxide,[7] especially in solutions containing organic substances.

With the application, however, of the concept of reaction velocity to a study of catalytically accelerated reactions, immense impetus was given to the analytical application of catalysis, both in its qualitative and quantitative aspects. The scope of the investigator was gradually extended by a variety of new catalytic reactions with which it was possible to demonstrate the presence and amount of acids and bases, and salts such as iodides. This development led naturally to a more fundamental and far-reaching study of the catalytic reactions, the influence of concentration, of non-essential materials which were present, of the retardation or negative catalysis that might occur, as well as to the mechanism whereby the acceleration of the reaction occurred. All of which has contributed to a very copious literature which it would be impossible, even in the scope of the whole of the present volume, to record and detail. It seems apposite, however,

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[1] Carstanjen, *Jacobsen's Chem. Techn. Report*, 1863, **2**, 92.

[2] *Hand. d. anal. chem.*, 1851, **2**, 775.

[3] Graeger, *Ann. Chim.*, 1859, **111**, 124; Mullen, *J. pr. Chem.*, 1860, **80**, 118.

[4] Kastner, *Zeitsch. angew. Chem.*, 1889, **2**, 205.

[5] *Analyst*, 1881, **6**, 36.

[6] *Traité des corps gras*, 1823.

[7] Ebell, *Zeitsch. d. Verein Deutsch. Ing.*, 1881, p. 26.

to outline the various broad developments of the application of catalysis to analytical chemistry and to do so in sections dealing respectively with catalysis in gas analysis, in inorganic and in organic analysis, both qualitative and quantitative, as well as in the applications of physico-chemical measurements.

CATALYSIS IN GAS ANALYSIS

(*a*) *Analytical combustion processes.*—The analysis of combustible gases by catalytic means is a matter of the utmost simplicity, when such combustible gases are present singly in a given mixture. Thus, hydrogen, in mixtures of non-combustible gases containing oxygen, may be estimated by combustion in the presence of finely divided palladium or palladised asbestos even at the ordinary temperature, though naturally the velocity is usually accelerated by raising the temperature by means of a small spirit lamp. This constitutes the modification by Lunge and by Hempel of the original investigations of Turner, previously cited, in which researches it was shown that with the aid of platinum balls (mixtures of clay and platinum) quite minute quantities of hydrogen or of oxygen in mixtures of the two could readily be determined, even in mixtures the concentrations of which were such that explosion methods were not available. The composition of the gas is readily deducible from the observed contraction.

In a similar manner, carbon monoxide may be determined by combustion with excess of oxygen in a heated capillary tube containing palladised asbestos, the percentage being determined in the absence of other combustibles by the contraction in volume observed after passage over the catalyst. In presence of hydrogen, the quantity of carbon monoxide consumed is readily obtained by absorption in alkalies of the carbon dioxide produced. The method in the case of both hydrogen and carbon monoxide is by no means restricted to the use of the platinum metals as catalytic agents, although these have mainly been employed in actual analytical practice. For it can readily be shown that many other agencies will effect the catalytic combustion of hydrogen or carbon monoxide. Thus copper oxide, when suitably prepared by alternate reduction and oxidation at low temperatures, will readily combust mixtures of these gases and oxygen or air at temperatures below 200°, whilst finely divided nickel is an extremely efficient catalyst for combustion of hydrogen and oxygen at comparatively low temperatures. Ignited bog-iron ore has also been employed for low temperature combustion of carbon monoxide and hydrogen.

Of the hydrocarbons, it was demonstrated by Henry that ethylene, when mixed with sufficient oxygen, began to burn in contact with platinum sponge at 250°, and was completely oxidised at 270°. He further found that methane began to combust at temperatures just above 290°. This observation, however, is in sharp contrast to the results of Richardt,[1] who found no combustion at 450°, and negligible combustion in a rapid stream of methane–air mixture through a palladium tube even at 600–650°. Coquillon[2] applied the method to the determination of methane in the air of coal mines, using electrically heated glowing platinum or palladium. The method was developed by Winkler[3] and by Dennis[4] with the view of avoiding combustion of nitrogen at the high temperatures attained by the platinum spirals during combustion. The same reaction was made use of by Liveing[5] in an effort to determine methane in suspected mine gas by comparison of the light intensities of two identical spirals heated by the same current, the one burning in air the other in the mine gas.

Normally the sulphur-containing gases present in illuminating and fuel gases are determined by a catalytic reduction process.[6] Their estimation, however, by a catalytic combustion process was worked out by Valentin,[7] who passed the gases admixed with air over platinum sponge heated to redness in a porcelain tube, the oxides of sulphur, both di- and tri-oxide being collected in absorption liquids, completely oxidised to sulphate, and then estimated. Various modifications of this procedure have been suggested.

(*b*) *Preferential combustion.*—The principal facts upon which

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[1] *J. f. Gasbeleucht.*, 1904, **47**, 566, 590.

[2] *Compt. rend.*, 1877, **84**, 458.

[3] *Lehr. d. techn. Gasanalyse*, 1901, p. 180.

[4] See Hempel's "Gas Analysis."

[5] *Phil. Mag.*, 1880, (v), **9**, 126.

[6] See p. 444.

[7] *Chem. News*, 1868, **17/18**, 89.

the preferential combustion of gases as employed in gas analysis are based have been already given in the preceding section. It is to Henry[1] that we owe the first fundamental investigations of the subject, and upon his methods are based the modern developments of the processes of preferential combustion, more especially as worked out by Hempel.[2] As, normally, absorption methods are used to eliminate such gases as carbon monoxide and the unsaturated hydrocarbons from the mixtures to be analysed, the main use of preferential combustion is in the analysis of mixtures of hydrogen and methane. For this purpose, Hempel substituted palladium for the platinum employed by Henry, and it was shown that at temperatures not greater than 100° the hydrogen could be burned without the simultaneous oxidation of any methane. Care must be exercised, however, that the reaction does not become so energetic as to cause local overheating, since, already at 200°, methane starts to react with oxygen. With natural gas, the methane is associated with ethane and occasionally even higher homologues. Fractional combustion, using palladium, is here also applicable ; the alternative method of Richardt,[3] using a heated palladium wire at carefully controlled temperatures, gave less favourable results.

Copper oxide at 250° will oxidise hydrogen preferentially, methane being completely unattacked,[4] and this method is frequently recommended, as it does not involve the addition of oxygen, and in the subsequent combustion of methane at a higher temperature the possibility of simultaneous combustion of nitrogen is eliminated. Obviously, in such circumstances the reaction is no longer catalytic, but it would doubtless emerge, on examination, that the preferential combustion could be conducted catalytically with copper oxide as contact agent if oxygen or air in excess were added.

In a recent paper,[5] Bancroft has given an admirable survey of the problem of preferential combustion, more especially from the viewpoint of selective action of the catalytic agent. As the question is not without considerable interest, not only

[1] *Loc. cit.*

[2] *Ber. deutsch. chem. Ges.*, 1879, **12**, 1006.

[3] *Zeitsch. anorg. Chem.*, 1904, **38**, 65.

[4] Jaeger, *J. f. Gasbeleucht.*, 1898, **41**, 764.

[5] *J. Physical Chem.*, 1917, **21**, 644.

from the standpoint of analytical chemistry, but also from the theoretical point of view and its possible technical applications, it is opportune here to summarise the conclusions reached and to outline briefly the possibilities which they suggest.

From a *résumé* of the work of Henry, Bancroft shows that, in contact with platinum, hydrogen burns more readily than ethylene, which in its turn is oxidised before methane. This is associated by Bancroft with the absorptive powers of the platinum for the several gases, hydrogen being the most strongly absorbed. From the observations of Lunge and Harbeck,[1] it is concluded that carbon monoxide is retained most tenaciously by platinum and that in consequence it burns more readily than hydrogen in contact with platinum, which is confirmed by the work of Henry on mixtures of carbon monoxide, hydrogen, and oxygen, at temperatures of 150° to 170°. Henry showed, however, that, when fired by the spark, the preponderance of oxygen was taken by the hydrogen, and not by the carbon monoxide, a result which was later confirmed by Bunsen.[2]

Discussing subsequently the researches of Bone and his co-workers,[3] Bancroft points out that the above conclusions are not to be considered anomalous. For Bone succeeded in showing that methane readily oxidises when heated with oxygen in borosilicate bulbs to between 300° to 400° at velocities enormously greater than does hydrogen under the same conditions. Experiments by Bone on the explosion of methane and hydrogen with quantities of oxygen inadequate for complete oxidation of both gases showed, moreover, that the methane disappeared preferentially in such circumstances. In other words, it appeared that methane was oxidised preferentially when burning away from a surface, and that hydrogen disappeared first in contact with agencies such as platinum or copper oxide. In other words, the nature of the contact surface determined the order of combustion, which conclusion is rendered more probable from the fact that, contrary to the results with borosilicate glass, hydrogen burns more readily than methane in contact with chamotte at 500°.

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[1] *Zeitsch. anorg. Chem.*, 1898, **16**, 50.

[2] *Ges. Abh.*, 1904,**2**, 586.

[3] *J. Chem. Soc.*, 1902, **81**, 535 *et ff.*

The influence of the contact agent is further emphasised from the researches of Calvert, who showed[1] that oxygen adsorbed by boxwood charcoal oxidises ethylene to carbon dioxide and water at the ordinary temperature; and since charcoal has little effect on a mixture of hydrogen and oxygen, it seems probable, according to Bancroft, that charcoal would cause preferential burning of ethylene in a mixture of ethylene and hydrogen. The conclusion is therefore reached that by suitable choice of catalytic agent it should be possible to realise all the various alternatives of preferential combustion. The extraordinary possibilities which such a conclusion would entail needs but little emphasis in order to be comprehended. For it is obvious that, granted a successful result from the search for a suitable catalytic contact agent, many industrial problems might find an easy solution. Thus it ought not to be impossible to find suitable agencies for the removal of small quantities of carbon monoxide from industrial hydrogen by processes of fractional combustion in which, by preferential conversion of the monoxide to carbon dioxide, the gas would be freed from an impurity of considerable disadvantage in many industrial operations. Nor, for example, is it too much to hope that organically combined sulphur compounds in illuminating gas could be removed, by preferential means, in contact with its particular and individual catalytic agent. A correct envisaging of the experimental demonstrations of Henry, now some ninety years old, may lead to the most fascinating of conclusions. In this connection, it may be observed that in technical practice there is already one example of preferential combustion in operation, namely, in the removal of sulphuretted hydrogen from illuminating gas, by bog iron ore absorption with simultaneous revivification *in situ* by addition of air. In this case, the hydrogen sulphide is preferentially oxidised at the ordinary temperature to sulphur. Doubtless, many other similar applications of preferential combustion await discovery by the facile investigator.

(*c*) *Gas analytical reduction processes.*—An important application of a catalytic reduction process in analytical work is to be noted in the method for determination of carbon-sulphur compounds in gases by reduction in presence of

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[1] *J. Chem. Soc.*, 1867, **20**, 293.

platinised pumice to hydrogen sulphide, this latter being subsequently determined by any suitable method. The reduction takes place in contact with the finely divided metal at temperatures as low as 300–350°. According to Lunge, however,[1] the method gives results of but moderate accuracy, since, if oxygen be present, oxidation of the hydrogen sulphide to sulphur occurs with consequent low results. The method is, however, rapid and convenient, which cannot be claimed for the usual "referee test" for total sulphur, in which a measured quantity of gas is burned in a small burner, the sulphuric acid in the products being absorbed and estimated.

By comparison with the discussion on the removal of combined sulphur on the technical scale, given in Chapter IV., it will be seen that the catalytic decomposition of carbon-sulphur compounds is not confined to the platinum metals, but that nickel and iron, oxide of iron, pumice, and fireclay all assist the reduction process, at, however, more elevated temperatures for quantitative results.

Vogel[2] recommended a catalytic process for the qualitative detection of combined sulphur in illuminating gas. The test consisted in passing the gas through a heated tube containing strips of copper to retain the sulphur which, on dissolving in nitric acid, gave a solution containing all the sulphur in the form of sulphate.

The method of Knorre and Arendt[3] for the determination of nitric oxide by reduction with hydrogen in a heated platinum capillary tube is another applied catalytic process. By slow passage through the heated tube, the reaction occurring is given by the equation:

$$2NO + 2H_2 = 2H_2O + N_2.$$

There is a possibility of error, however, in that the reaction, if conducted too quickly, may proceed to the production of some ammonia, with consequent variation of the volume relationships upon which the method of estimation is based.

In a similar manner, nitrous oxide may be estimated, the reaction occurring being:

$$N_2O + H_2 = H_2O + N_2.$$

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[1] "Technical Gas Analysis," 1914, p. 256.

[2] *Ber.*, 1869, **2**, 741.

[3] *Ibid.*, 1899, **32**, 2136; 1900, **33**, 32.

Owing to the difference in the two volume changes, this method can be applied to a mixture of both nitrous and nitric oxides.

According to Treadwell,[1] Pollak has shown that carbon monoxide may be used as the reducing agent for nitric oxide provided the carbon dioxide be absorbed as it is formed.

(*d*) *Dissociation processes.*—The catalytic dissociation of nitrous oxide into its component elements has been recommended by Winkler,[2] cited by Woker.[3] The gas, when passed through a heated platinum capillary, is converted into nitrogen and oxygen :

$$2N_2O = 2N_2 + O_2,$$

and from the increase in volume the quantity of nitrous oxide may be determined. Obviously, however, if hydrogen be present, the previously discussed reduction will occur.

As is well known, most metals, even at the ordinary temperature, accelerate the decomposition of ozone, or are converted by it to peroxides. Thus the action is marked in the case of mercury, which, after treatment therewith, adheres in thin films to a glass-containing vessel. The conversion of bright metallic silver to a black superoxide is employed as a method of detection of the gas. Lead, copper, nickel, and cobalt are similarly attacked, as well as many of the lower oxides, which are converted to peroxides, as, for example, lead and manganous oxides. Manchot[4] has studied, in connection with the action of silver, the catalytic acceleration of the process by the presence of iron, and has shown that the minutest traces of this metal, preferably in the form of oxide, facilitate both the formation of the black peroxide and also the subsequent decomposition of the remaining ozone by means of the peroxide. The blackening is obvious, even in solutions containing but one part of ozone in 10,000 parts of the solution, and with its aid the presence of ozone in the hotter parts of gas flames is readily demonstrable.

Ozone in presence of finely divided platinum is completely decomposed, yielding oxygen. With this fact in view, Tom-

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[1] Vol. II, p. 567.

[2] "Anleit z. chem. Untersuch. d. Industriegase," 1893, p. 427.

[3] "Katalyse in d. anal. Chem.," 1915, p. 347.

[4] *Ber.*, 1906, **39**, 3510 ; 1907, **40**, 2891 ; 1908, **42**, 3948.

masi[1] suggested the determination of ozone in presence of chlorine and nitrous acid by the difference in titration of two standard ferrocyanide solutions when treated with samples of gas, with and without the previous decomposition process with platinum sponge.

A case of preferential decomposition studied by Richter[2] illustrates the analytical application of catalysis by nickel. It was shown that in a mixture of ethane, methane, and hydrogen the action of a heated nickel spiral brought about the decomposition of ethane to carbon and hydrogen. The methane, however, is slightly attacked if the reaction be carried to completeness. The tendency of ethane to decomposition into the elements is illustrated by Bone's experiment,[3] in which an explosion of a mixture of ethane and insufficient oxygen yielded a dense cloud of carbon. Mixtures of ethylene, hydrogen, and oxygen, and of acetylene, hydrogen and oxygen with the same total carbon : hydrogen : oxygen ratio as in the ethane experiments, yielded practically completely carbon monoxide and hydrogen with little or no steam formation —another example of preferential combustion similar to those previously discussed.

(*e*) *Absorption processes.*—In the absorption processes of gas analysis, by far the most important case of catalysis is one of negative catalysis, the retarding action of gases on the absorption of oxygen by phosphorus. In the analysis of coal gas, it is well known that the use of the phosphorus absorption pipette is not advisable, since traces of unsaturated hydrocarbons paralyse the activity of the phosphorus. Lunge[4] states that among the substances interfering with the absorption of oxygen are, according to Davy, Graham, and Vogel, hydrogen sulphide and phosphide, carbon disulphide, sulphur dioxide, iodine, bromine, chlorine, nitrogen peroxide, ethylene, acetylene, ether, alcohol, petroleum, oil of turpentine, cupione, creosote, benzene, ammonia, alcohol, tar, and many essential oils. Ethylene in concentration of 0·25 per cent. by volume, it is further stated, is sufficient to produce the effect. Haber[5]

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[1] *Chem. News*, 1879, **29**, 284.

[2] *Diss.*, Dresden, 1909.

[3] *Proc. Roy. Inst.*, 1908, **19**, 82.

[4] "Technical Gas Analysis," 1914, p. 121.

[5] "Habilitations arbeit," Munich, 1896, p. 97.

found 0·17 per cent. sufficient, while Hempel is of opinion that 0·04 per cent. is sufficient. A considerable controversy has revolved around the supposed retarding action of methane and the higher saturated hydrocarbons. The experiments of Brunck, however, would seem to oppose the view that these act as negative catalysts, since it is stated that the disturbing substances can, in most cases, be removed by previous treatment of the gas with fuming sulphuric acid.

The mechanism of the retarding action is quite unexplained. Centnerszwer[1] associates the action with the unsaturated character of the negative catalysts. Bancroft,[2] in a general discussion of catalyst poisons, shows that it is possible to "account for all the cases that have been considered if we postulate suitable and not improbable adsorptions," the poison being preferentially adsorbed and decreasing the normal adsorption in absence of the poison. The case of phosphorus, however, is not included in Bancroft's survey.

An error in the oxygen estimation by phosphorus absorption may be attributed to catalytic influence. It is found, according to Baumann,[3] and Leeds [4] that carbon monoxide is oxidised by oxygen to carbon dioxide in presence of phosphorus. This was denied by Remsen and Keiser,[5] but reiterated later by Baumann[6] and by Boussingault,[7] who, however, showed that the amount was exceedingly small, and has been attributed to the ozonising action of phosphorus on oxygen.

Of catalytic accelerators in absorption processes, mention may first be made of the addition of alkali to pyrogallol in order to promote the rate of absorption of oxygen. Originally discovered by Döbereiner, it was introduced into gas analysis by Liebig, and provides an absorption agent of high efficiency. The addition of mercury sublimate to alkaline solutions of pyrogallol in order to accelerate the absorption of oxygen has also been proposed.[8] Its use, however, increases the possibility of carbon monoxide formation from the pyrogallol,

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[1] *Zeitsch. physikal. Chem.*, 1898, **26**, 21.

[2] *J. Physical Chem.*, 1917, **21**, 734.

[3] *Ber.*, 1883, **16**, 1146.

[4] *Chem. News*, 1883, **48**, 25.

[5] *Amer. Chem. J.*, 1883, **4**, 454.

[6] *Ber.*, 1884, **17**, 283.

[7] *Compt. rend.*, 1864, **58**, 777.

[8] Stassana, *Compt. rend. Soc. Biol.*, 1905, **58**, 96.

which has been shown by a number of investigators[1] to hinder exact work, unless the carbon monoxide can be removed prior to the taking of the volume reading.

The addition of vanadic oxide or of uranyl sulphate to strong sulphuric acid (sp. gr. 1·84) is recommended by Lebeau and Damiens[2] as a rapid absorption agent for olefines in place of fuming sulphuric acid.

CATALYSIS IN INORGANIC ANALYSIS

(*a*) *Oxidation processes.*—Of considerable importance in analytical technique and at the same time of great interest from the theoretical point of view is a series of volumetric operations in which potassium permanganate is employed as oxidising agent. The catalytic influence of manganese sulphate in all these reactions has long been known and studied. Thus, Harcourt and Esson[3] observed the accelerating action of manganese sulphate formed during the reaction between potassium permanganate and oxalic acid, when conducted in presence of sulphuric acid. A study of the kinetics of the process was made, in which it was shown that, for a given time interval, the velocity of reaction, in presence of a constant quantity of permanganate but with varying amounts of oxalic acid, sulphuric acid, and manganese sulphate, was proportional to the amounts of sulphuric acid and manganese sulphate initially present, and also dependent on the quantity of oxalic acid, but in no simple proportionality. It was shown that, with oxalic acid in excess, permanganate disappeared with time in accordance with the monomolecular law.

At a much later period, Schilow reinvestigated the reaction kinetics.[4] He showed that with the oxalic acid in great excess the progress of the reaction can be expressed by the velocity equation

$$\frac{dx}{dt} = k(a - x)x,$$

where a denotes the original permanganate concentration, and x the amount converted into manganese sulphate in the

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[1] See Clowes, *Zeitsch. anal. Chem.*, 1897, **36**, 504.

[2] *Compt. rend.*, 1913, **156**, 557.

[3] *Phil. Trans.*, 1866, **156**, 201.

[4] *Ber.*, 1903, **36**, 2735.

time t. With initial concentration, b, of manganese sulphate, the reaction equation would therefore be

$$\frac{dx}{dt} = k(b + x)(a - x).$$

It can be readily demonstrated mathematically in regard to the former of these two equations that the maximum velocity is attained when

$$x = \frac{a}{2},$$

and in the second case the same is true when

$$x = \frac{a - b}{2}.$$

This conclusion was experimentally verified in both cases, it being shown that, starting slowly, the rate of reaction steadily increased, until, at the period of half-decomposition, it attained its maximum and then fell away. The plot of an experimental curve in an experiment in initial absence of manganese sulphate is given in Fig. 32. The reaction forms, therefore, a beautiful example of induction, in which it must be observed that the phenomenon is due to the auto-production of catalytic agents, and not, as in the hydrogen–chlorine combination, to the progressive displacement of retarding agents.

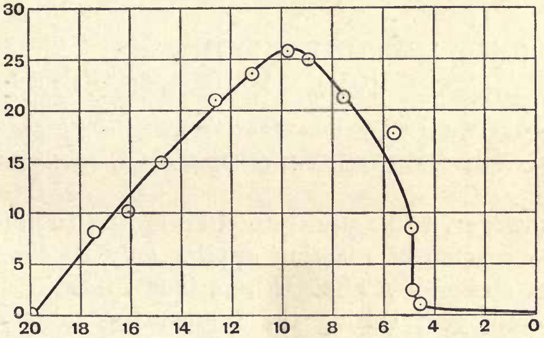
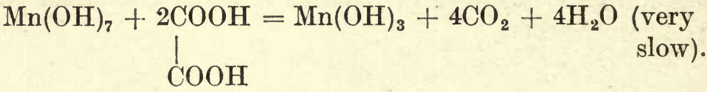
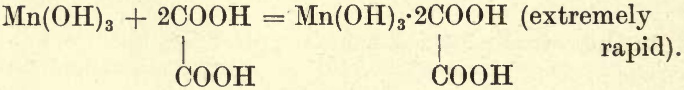


FIG. 32.

Schilow concluded from these studies that the concentration of oxalate, so long as it was in excess, practically did not influence the reaction, and that what was being measured was the velocity of the reaction between the higher and lower states of oxidation of manganese. The equations representing this view would be :

(1) 

$$\mathrm{Mn(OH)_7} + 2\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} = \mathrm{Mn(OH)_3} + 4\mathrm{CO_2} + 4\mathrm{H_2O} \text{ (very slow).}$$

(2) 

$$\mathrm{Mn(OH)_3} + 2\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} = \mathrm{Mn(OH)_3}\cdot 2\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \text{ (extremely rapid).}$$

$$\text{(3) } \mathrm{Mn(OH)_7} + \mathrm{Mn(OH)_3}\cdot 2(\mathrm{COOH})_2 = 2\mathrm{Mn(OH)_3} + 4\mathrm{CO_2} + 4\mathrm{H_2O} \text{ (measured).}$$

The last reaction apparently, according to Schilow, may represent the sum of two successive reactions :

$$\text{(3}a\text{) } \mathrm{Mn(OH)_7} + \mathrm{Mn(OH)_3}\cdot 2(\mathrm{COOH})_2 = \mathrm{Mn(OH)_6} + \mathrm{Mn(OH)_4}\cdot 2(\mathrm{COOH})_2 \text{ (measured).}$$

$$\text{(3}b\text{) } \mathrm{Mn(OH)_4}\cdot 2(\mathrm{COOH})_2 + \mathrm{Mn(OH)_6} = 2\mathrm{Mn(OH)_3} + 4\mathrm{CO_2} + 4\mathrm{H_2O} \text{ (extremely rapid).}$$

It is, however, to be understood according to Schilow, that the above scheme of reaction applies only to the particular conditions chosen by him. Alterations in the acid concentrations employed, raising the temperature above 25°, and the addition of catalysts such as iron, chromium, and silver salts, would all tend to increase the velocity of the first reaction, and lead, therefore, to a different velocity equation of the form :

$$\frac{dx}{dt} = k_1(a - x)^n(c - x)^m + k_3x(a - x),$$

c in this equation referring to the concentration of oxalate, k_1 and k_3 to the constants of the equations 1 and 3.

Schilow extended these studies[1] in his researches on the

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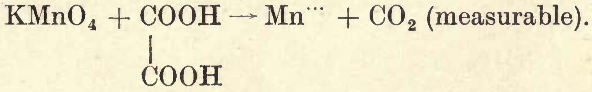
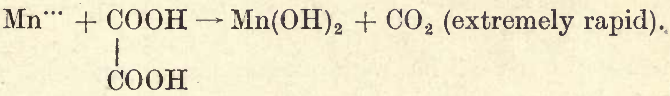
[1] *Zeitsch. physikal. Chem.*, 1903, **42**, 661.

coupling of chemical reactions, and concludes that the above conclusions are applicable generally to permanganate oxidation of such oxy-acids, *e.g.*, tartaric acid, as show a tendency towards complex formation.

A somewhat different conclusion is reached by Skrabal.[1] He assumes, like Schilow, an intermediate stage of oxidation and an intermediate product, the manganic ion, which reacts with oxalic acid more rapidly than the permanganic ion. He distinguishes three periods in the reaction : (1) The incubation period, in which permanganate and oxalic acid interact to give carbon dioxide and manganic ion, which latter reacts extremely rapidly with further oxalic acid to give the manganous salt and more carbon dioxide. The reactions would be



$$KMnO_4 + \begin{array}{c}COOH\\ | \\ COOH\end{array} \rightarrow Mn^{\cdot\cdot\cdot} + CO_2 \text{ (measurable).}$$

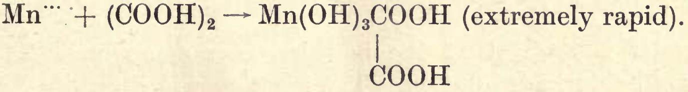


$$Mn^{\cdot\cdot\cdot} + \begin{array}{c}COOH\\ | \\ COOH\end{array} \rightarrow Mn(OH)_2 + CO_2 \text{ (extremely rapid).}$$

(2) The period of induction, in which the manganous oxide and permanganate interact to yield the manganic ion, which reacts, as above, but which tends also to form an oxalate complex and the oxidation stages Mn^{II} and Mn^{IV} according to the scheme :

$$Mn(OH)_2 + KMnO_4 \rightarrow Mn^{\cdot\cdot\cdot} \text{ (less rapid).}$$

$$Mn^{\cdot\cdot\cdot} + (COOH)_2 \rightarrow Mn(OH)_2 + CO_2 \text{ (extremely rapid).}$$



$$Mn^{\cdot\cdot\cdot} + (COOH)_2 \rightarrow Mn(OH)_3\begin{array}{c}COOH\\ | \\ COOH\end{array} \text{ (extremely rapid).}$$

$$Mn^{\cdot\cdot\cdot} \rightarrow Mn(OH)_2 + Mn(OH)_4 \text{ (extremely rapid).}$$

(3) The end period, which is twofold in nature, corresponding with the disappearance of the manganic–oxalate complex and of the conversion of Mn^{II} and Mn^{IV} to manganous oxide,

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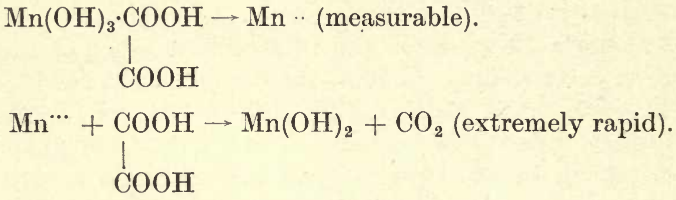
[1] *Zeitsch. anal. Chem.*, 1903, **42**, 329 ; *Zeitsch. anorg. Chem.*, 1904, **42**, 60 ; *Zeitsch. Elektrochem.*, 1905, **11**, 653.

the retardation in the end period being attributed to the slow decomposition of the manganic–oxalate complex.

End period (*a*).

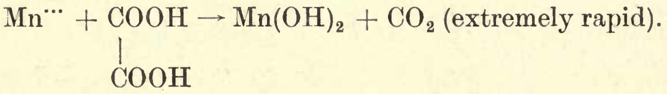


$$\mathrm{Mn(OH)_3\cdot\begin{array}[t]{c}COOH\\|\\COOH\end{array}} \rightarrow \mathrm{Mn^{\cdot\cdot}}\ \text{(measurable).}$$

$$\mathrm{Mn^{\cdot\cdot\cdot}} + \mathrm{\begin{array}[t]{c}COOH\\|\\COOH\end{array}} \rightarrow \mathrm{Mn(OH)_2} + \mathrm{CO_2}\ \text{(extremely rapid).}$$

End Period (*b*).

$$\mathrm{Mn(OH)_2} + \mathrm{Mn(OH)_4} \rightarrow \mathrm{Mn^{\cdot\cdot\cdot}}\ \text{(less rapid).}$$



$$\mathrm{Mn^{\cdot\cdot\cdot}} + \mathrm{\begin{array}[t]{c}COOH\\|\\COOH\end{array}} \rightarrow \mathrm{Mn(OH)_2} + \mathrm{CO_2}\ \text{(extremely rapid).}$$

The permanganate titration of iron in presence of hydrochloric acid.—Löwenthal and Lennsen[1] showed that in titrating ferrous iron with permanganate solution, more permanganate was required than theory demands if the iron solution was acidified with hydrochloric acid and that this could be explained as being due to an induced reaction of the type studied by Kessler.[2] Interaction occurred between the hydrochloric and permanganate with production of chlorine, thus using permanganate in excess of that required by the iron. This reaction, which ordinarily would not occur, is induced by the simultaneous oxidation of the ferrous salt, the reaction being representable by the equation :

$$16\mathrm{HCl} + 2\mathrm{KMnO_4} = 2\mathrm{KCl} + 2\mathrm{MnCl_2} + 5\mathrm{Cl_2} + 2\mathrm{H_2O}.$$

Kessler showed[3] that the addition of manganous salts prevented chlorine evolution. The reaction was carefully studied by Skrabal,[4] who associated the chlorine production, as had Zimmermann previously,[5] with the formation by the permanganate of a higher oxide of iron, which, according to

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[1] *Zeitsch. anal. Chem.*, 1861, **1**, 329 ; *J. pr. Chem.*, 1862, **86**, 193.

[2] *Pogg. Ann.*, 1855–1863, **95**, **96**, **113**, **118**, **119**.

[3] *Ibid.*, 1863, **118**, 48 ; **119**, 225.

[4] *Zeitsch. anal. Chem.*, 1903, **42**, 359 ; *Zeitsch. anorg. Chem.*, 1904, **42**, 48, 76.

[5] *Ber.*, 1881, **14**, 779 ; *Zeitsch. anal. Chem.*, 1882, **21**, 307.

Manchot,[1] was to be regarded as Fe_2O_5. The two reactions occurring would therefore be (*a*) the main reaction :

$$Fe_2O_5 + 4Fe = 3Fe_2O_3,$$

and (*b*) the induced reaction,

$$Fe_2O_5 + 4HCl = Fe_2O_3 + 2H_2O + 2Cl_2.$$

Within limits, it was shown that, with rising ferrous ion concentration and decreasing hydrochloric acid concentration, the excess permanganate required was decreased.

The addition of manganous sulphate, it was shown, corrected the tendency to chlorine production, not by a retarding influence on the induced reaction, but by its strongly catalytic effect on the iron oxidation process, giving it a velocity so great that negligible quantities only of hydrochloric acid have the time to oxidise. Skrabal showed that the theoretical aspects of the oxidation process gave results as to mode of operation which were in substantial agreement with those actually found in analytical practice.

Treadwell gives data of Zimmermann and Reinhardt for permanganate titration of vanadium in presence of absence of iron. Müller and Diefenthäler[2] carry out the process in hydrochloric acid solution with addition of manganous salts, which accelerate the primary reaction as in the case of iron just considered. The corresponding reactions with tungsten and molybdenum were investigated by van der Pfordten.[3] Follenius[4] showed that with uranium salts the same induced reaction occurs, and Zimmermann[5] showed the importance of addition of the manganous salts in the titration process. In the well-known Volhard method for permanganate determination of manganese,[6] which subsequently has been modified by a considerable number of analysts, manganese sulphate acts similarly as an accelerator, the reaction occurring according to the general equation :

$$2MnO_4' + 3Mn^{\cdot\cdot} + 2H_2O \rightarrow 5MnO_2 + 4H^{\cdot}.$$

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[1] *Annalen*, 1902, **325**, 93.

[2] *Zeitsch. anorg. Chem.*, 1911, **71**, 343.

[3] *Ann. Chim.* 1884, **222**, 137 ; *Zeitsch. anal. Chem.*, 1884, **23**, 413.

[4] *Zeitsch. anal. Chem.*, 1872, **11**, 179.

[5] *Ann. Chim.*, 1882, **213**, 285.

[6] *Ibid.*, 1879, **198**, 318.

In the previously cited research of Skrabal,[1] a theoretical investigation is made of the low results which may be obtained. These latter are due to the incompleteness of the oxidation of the manganese to dioxide, owing to simultaneous precipitation of unoxidised manganous oxide with the dioxide. According to Skrabal, this precipitation tends to occur owing to the decomposition of the manganic oxide formed in the first stages of oxidation :

$$4Mn^{\cdot\cdot} + MnO_4' + 8H' = 5Mn^{\cdot\cdot\cdot} + 4H_2O,$$

the trivalent manganese then decomposes according to equation :

$$2Mn^{\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot\cdot\cdot} + Mn^{\cdot\cdot}.$$

The analytical methods employed have, as their aim, the suppression of the precipitation of the manganous oxide, which reacts with further quantities of permanganate until completely converted into the dioxide.

Finally, the same catalytic phenomenon is to be observed in the titration of hydrogen peroxide solutions with permanganate, and in the titration of sulphites. In the latter case, Honig and Zatsek[2] express the opinion that low results are due to formation of a certain amount of dithionate, which Milbauer[3] proposes to suppress by working with excess of permanganate, strongly acidified with sulphuric acid, to which the sulphite solution is added, the excess permanganate being titrated by oxalic acid solution.

Ferrous sulphate may be employed as accelerator in the qualitative test for hydrogen peroxide. The liberation of iodine from potassium iodide solutions by hydrogen peroxide is ordinarily an extremely slow process ; by addition of ferrous sulphate, the reaction proceeds rapidly, and is also extremely sensitive, so that minute traces of the peroxide may be detected.[4] The peroxide–iodide reaction is negatively catalysed by acids, and does not occur, even in presence of ferrous sulphate, in acid solutions. If, however, a ferrous–copper sulphate mixture is employed, the sensitivity of the test is restored, a remarkable case of activation.

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[1] *Zeitsch. anorg. Chem.*, 1904, **42**, 60.

[2] *Monatsh.*, 1887, **4**, 738.

[3] *Zeitsch. anal. Chem.*, 1909, **48**, 17.

[4] Schönbein, *J. pr. Chem.*, 1859, **79**, 66.

Price[1] noted the catalytic activity of ferrous sulphate in the interaction of potassium persulphate and potassium iodide,

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

showing that the normal bimolecular reaction was accelerated proportionately to the concentration of the catalyst, yielding, therefore, a velocity equation of the form

$$\frac{dx}{dt} = k.c.(a - x)(b - x),$$

where c denoted the concentration of catalyst, and a and b the initial concentrations of the reactants. The reaction occurring may be applied to the analytical determination of the persulphate.

Of further oxidation processes in analytical chemistry in which catalytic activity is invoked, mention may be made of the influence of alkalis in promoting oxidation processes. Thus, the oxidation of the arsenious to the arsenic stage by chlorine and bromine takes place rapidly in alkaline solutions.

Reduction processes.—In the operation of reduction processes in chemical analysis with the hydrogen evolved by interaction of metals and acids or alkalies, the catalytic *rôle* is well illustrated.

As is well known, nitrates, nitrites, and chlorates may all be determined analytically by reduction, in the first two cases to ammonia, in the last to chloride, followed by subsequent estimation of the reduced product. Further, the reduction of solutions containing iron salts, prior to estimation by permanganate, is also an analytical operation of frequent and important use. To effect the reduction, numerous methods of generating the hydrogen have been adopted, both in acid and in alkaline solutions.

For the reduction of nitrates in acid solutions zinc was originally employed as reducing agent; but, owing to the tendency which is exhibited by this metal to yield the easily decomposed nitrous acid and the consequent errors due to loss of nitrogen, zinc has been abandoned in favour of iron. Ulsch[2]

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[1] *Zeitsch. physikal. Chem.*, 1898, **27**, 474.

[2] *Zeit. anal. Chem.*, 1891, **30**, 175.

showed that reduction of nitrates, using iron and sulphuric acid, yielded ammonia quantitatively without the formation of the intermediate products. It was found also that the ferrous sulphate produced in the course of the reaction :

$$2KNO_3 + 8Fe + 10H_2SO_4 \\ = K_2SO_4 + 8FeSO_4 + (NH_4)_2SO_4 + 6H_2O,$$

accelerated the reducing action in marked degree.

In addition, however, to the catalytic influence of the reaction products, the reduction phase may also be modified by the use of activated metals as agents for hydrogen production. In the case of zinc, it was shown by Williams[1] that in the determination of nitrates in water the substitution of a zinc–copper couple, as originally employed by Gladstone and Tribe, for the ordinary zinc dust gave a reagent extraordinarily well suited to the purposes of reduction, and capable of further acceleration by addition of neutral salts and dilute acids. Ulsch[2] showed that the corresponding copper–iron couple was a more active agent than iron alone, and in suitable circumstances could be operated at the ordinary temperature. The use of such an agent also possesses the advantage that the ferrous sulphate formed neutralises the negatively catalytic effects which chlorides exert in the reduction of the nitrates. Schmidt[3] employed a zinc–iron mixture in acid solutions.

In a similar manner, the use of the zinc–copper couple as agent for the reduction of chlorates to chlorides has been studied and recommended by Thorpe and Eccles[4] and by Bothamley and Thompson.[5]

The reduction of solutions of ferric salts by zinc amalgam in sulphuric acid solution is another application of the activated metal in analytical chemistry. Müller and Wegelin[6] show that the reducing agent is eight to nine times more completely used in the case of the amalgam than with pure zinc, although the reaction velocity is slower. By addition of copper sulphate solutions in minimal amounts, the reaction velocity of the amalgam may be so far accelerated as to overcome this dis-

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[1] *Analyst*, 1881, **6**, 36.

[2] *Loc. cit.*

[3] *Chem.-Zeit.*, 1893, **17**, 173.

[4] *J. Chem. Soc.*, 1873, **26**, 541.

[5] *Ibid.*, 1888, **53**, 164.

[6] *Zeitsch. anal. Chem.*, 1911, **50**, 615.

advantage. Copper and silver in the metallic state, according to Müller and Wegelin, also catalyse the reduction of iron by zinc amalgam, presumably by interaction of the metal with ferric iron,

$$Cu + Fe^{\cdot\cdot\cdot} = Fe^{\cdot\cdot} + Cu^{\cdot},$$

and subsequent reduction to the metallic state of the zinc.

In the alkaline reduction of nitrates it was shown by Vernon Harcourt[1] that, using zinc and aqueous potash as reducing agent, only three-quarters of the nitrate was converted into ammonia. On the other hand, if a mixture of zinc and iron was employed, reduction was complete. In place of the zinc–iron mixture, zinc slightly covered with a coating of copper has also been employed.

Reduction in alkaline solution with aluminium results in complete conversion of nitrates to ammonia. Modern developments of the alkaline method, however, mainly employ a ternary alloy of aluminium, copper, and zinc, known as Devarda's alloy, after the inventor.[2] The original alloy was composed of 50 parts of copper, 45 parts of aluminium and 5 parts of zinc. Later specifications suggest 39 parts of copper, 59 parts of aluminium and 2 parts of zinc. The attack by alkali is very rapid and energetic, and after a half-hour's reduction distillation of the ammonia may be undertaken with quantitative results.

The use of sodium amalgam for reduction of nitrates is yet another application of the principle of activation.

The theoretical explanation of the principle of activation is to be sought largely in the electro-chemical behaviour of such alloys as compared with the single metals. As such, the matter has been fully treated elsewhere (Chap. XII., p. 394), and so it is not necessary here again to enlarge upon the point. A further factor of possible influence has been emphasised by Bödländer,[3] who associates catalytic activity in such cases with the rate and state of evolution of hydrogen from such metallic couples. It is at the metal surfaces that the reduction undoubtedly occurs, and the nature and com-

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[1] *J. Chem. Soc.*, 1862, **15**, 385; 1863, **16**, 289.

[2] *Chem.-Zeit.*, 1892, **16**, 1952.

[3] *Fifth Int. Cong. App. Chem.*, 1903, p. 635.

position of such surfaces may determine the nature of the hydrogen evolution and the participation of the gas in the reducing action.

CATALYSIS IN ORGANIC ANALYSIS

(*a*) *Elementary analysis.*—Historically considered, the most important application of catalysis in organic analysis is to be found in the determination of the composition of organic compounds by methods of combustion. The familiar method of determining carbon and hydrogen in such materials by combustion with oxygen in presence of copper oxide is at once a classical example of catalysis and an operation of fundamental import to the organic chemist. Gay-Lussac in 1816 employed copper oxide in the analysis of uric acid and the process was immediately tested and found applicable by Döbereiner, Prout and Beraud.[1] In all these cases, however, the material to be analysed was mixed intimately with the copper oxide and thus brought to combustion. The modern developments of the process date from the time of Liebig, whose investigations of the operation, determined the lines of subsequent procedure, converting the process to one of combustion of the organic compound with oxygen in presence of the copper oxide as catalyst.

Modifications of the copper oxide method have been largely developed during the past two decades, more especially in the direction of substituting for copper oxide, platinum, in suitable form, as contact agent. The adoption in many present-day laboratories of the simplified method of analysis due to Dennstedt is evidence for the progress which such modifications have made.

The high activity of suitably prepared platinum in the oxidation of the products of organic combustion was demonstrated by Kopfer.[2] He employed a mixture of platinum black and asbestos in order to obtain a maximum surface effect for the contact material, and with substances containing carbon, hydrogen, and oxygen only, a combustion tube containing the substance in a boat followed by the platinum

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[1] *Schweigger's J.*, 1816, **16**, **17**; 1818, **22**; 1820, **29**.

[2] *Zeitsch. anal. Chem.*, 1878, **17**.

asbestos is all that is required besides the usual absorption agents for carbon dioxide and water. With nitrogen-, sulphur-, and halogen-containing bodies the usual absorption agents for such substances were required.

Claesson[1] utilised heated platinum in a method for determining sulphur in organic compounds. The substance was burnt in an atmosphere of oxygen containing oxides of nitrogen, which, on subsequent contact with heated platinum, oxidised the sulphur to sulphuric acid, which could then be absorbed in water and estimated. Claesson extended the process to the determination of halogens, and this was likewise proposed by Schwarz[2] for the determination of bromine, and by Zulkowsky and Lepéz[3] for halogens generally. These latter suggested platinised quartz as contact material, the absorption agent being ammoniacal hydrogen peroxide, which absorbed all the halogen acid produced in the process and reduced any free halogen formed to the corresponding acid, according to the equation:

$$H_2O_2 + X_2 = 2HX + O_2.$$

Various experimental modifications of the use of platinum were made from time to time. Thus, the use of platinum combustion tubes was recommended[4] without, however, any considerable development. Electrical heating of platinum spirals has frequently been recommended.[5] The elaboration of the method of organic analysis, employing platinum as contact material, is due, however, mainly to the researches of Dennstedt, who has succeeded in perfecting a method of analysis of organic compounds whereby, in one operation, carbon, hydrogen, nitrogen, sulphur, and halogen may all be estimated.

The essential principles upon which the Dennstedt method of analysis is based may be here outlined, the actual experimental details being, however, eliminated, since these are readily obtainable in the modern texts of practical organic

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[1] *Zeitsch. anal. Chem.*, 1883, **22**, 177; *Ber.*, 1886, **19**, 1910; 1887, **20**, 3065.

[2] *Monatsh.*, 1882, **3**, 726.

[3] *Ibid.*, 1884, **5**, 537.

[4] Gooch, *Am. Chem. J.*, 1880–1888, **2**, 247; Dudley, *ibid.*, 1888, **10**, 433.

[5] Carrasco and Planchen, *Gazzetta*, 1906, **36**, 492; Breleau and Leroux, *Compt. rend.*, 1907, **145**, 524; Milschsack and Roth, *Zeitsch. angew. Chem.*, 1914, **27**, 5.

chemistry as well as in the original literature.[1] The contact material originally employed was composed of platinum (obtained by ignition of the pyridine double salt), or of platinised quartz. Later, use was made of thin pieces of platinum foil, star-shaped and fitted on to a central strip of foil 6 to 8 centimetres long. The advantage of using foil over the finely divided preparations lies in the fact that minimal amounts only of sulphuric acid are retained by the foil whereas using platinised asbestos marked amounts of the acid may be occluded. In the earlier forms of apparatus some few centimetres beyond the contact mass, in the combustion tube, were placed two weighed boats containing finely divided silver, which, in the operation of the process, were heated to *ca.* 300° and served to retain halogens and the sulphur which, in the course of the oxidation process, had been converted to sulphuric acid. Beyond these boats were placed two weighed porcelain boats filled with lead superoxide to absorb any sulphurous acid and nitrogen dioxide. As was first shown by Henry,[2] lead superoxide may be used as absorption agent in sulphur determinations, and Warren[3] utilised this absorption for quantitative determinations. Kopfer employed the same material for retaining oxides of nitrogen. The operating temperature for the lead peroxide is *ca.* 150°. Calcium chloride and potash or soda-lime absorption apparatus are attached to the combustion tube for determination of water and carbon dioxide. The addition of a bubbler containing palladium chloride solution to the end of the apparatus serves as an indicator that combustion is complete, since incomplete oxidation causes a blackening of the solution, due to reduction.

If, in addition to carbon, hydrogen, and oxygen, halogens alone are present, the increase in weight of the vessels containing silver gives the amount of halogen present. If nitrogen be present but not sulphur, the increase in weight of the lead

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[1] See, for example, Dennstedt, "Die Entwicklung der Organischen Elementaranalyse." *Ahrens Sammlung*, Bd. **4**, Stuttgart, 1899; "Anleitung zur vereinfachten Elementaranalyse," Hamburg, 1906; *Zeitsch. angew. Chem.*, 1897, **10**, 462; 1904, **17**, 30; 1905, **18**, 320, 1134, 1562; *Zeitsch. anal. Chem.*, 1901, **40**, 612; 1902, **41**, 525; 1903, **42**, 417; 1906, **45**, 26; 1907, **46**, 26; *Ber.*, 1897, **30**, 1592; 1905, **38**, 3730; 1906, **39**, 1623; 1907, **40**, 3677, 4300; 1908, **41**, 600, 2778.

[2] *J. Pharm. Chim.*, 1849, **20**, 59.

[3] *Zeitsch. anal. Chem.*, 1866, **5**, 169.

peroxide corresponds with the amount of nitrogen present. Sulphur, when present, is divided between the vessels containing silver and the lead peroxide, and when associated in the original material with halogen and nitrogen must be separated therefrom in the two cases. This is effected thus: the sulphur is present in the vessels containing silver as the sulphate and is separated from the halides by digestion of the silver with water, whereby the sulphate is dissolved, and may then be added to the sulphate in the superoxide. The halogens are then extracted from the silver by means of potassium cyanide and determined in the usual gravimetric manner after elimination of the cyanide by boiling with nitric acid. For the determination of sulphur and nitrogen in the lead peroxide, the residue after combustion is extracted with 33 per cent. alcohol in which the sulphate is precipitated. The alcoholic extract is made up to 100 c.c. and an aliquot portion thereof evaporated to give the quantity of nitrate present.

In later modifications of the Dennstedt process, it has been found advantageous to eliminate the silver vessels in all cases except those in which iodine is to be estimated. Bromine and chlorine are absorbed quite conveniently by lead peroxide; iodine, however, is not retained. In substances containing nitrogen, sulphur, chlorine, and bromine, the lead peroxide is extracted with sodium carbonate or bicarbonate solution (3–4 per cent.) in the cold for twenty-four hours, or for several hours in a shaking machine. The filtrate is then divided into aliquot portions, which are then separately analysed for sulphur, by precipitation as sulphate, and for halogens, by precipitation as the silver halide, the nitrogen if present being obtainable by difference.

Halogen estimations in organic compounds. — An elegant application of catalytic hydrogenation to the determination of halogens in organic compounds is of quite recent date. It was shown by Borsche and Heimburger[1] that organic halogen compounds when heated with hydrogen in presence of the colloidal platinum metals were converted to the hydrogenated products with simultaneous liberation of the halogen acid. This reaction was applied by Busch and Stove[2] to the

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[1] *Ber.*, 1915, **48**, 452, 850.

[2] *Ibid.*, 1916, **49**, 1063.

analytical estimation of halogens in such compounds, using palladium deposited on calcium carbonate as the catalytic agent. The liberated acid was neutralised as formed by alkali present in the aqueous or alcoholic solution of the compound. Solvents such as benzene and acetone were found to inhibit the catalytic activity of the metal. The halogen, after liberation from the organic material, was estimated by simple titration. It was claimed that, by the use of calcium carbonate as support material for the catalytic agent, recovery of the metal was facilitated, thus minimising expense. Subsequent researches, however, of C. Kelber[1] showed that nickel could be used as an excellent substitute for platinum and palladium colloids as catalytic agent, thereby eliminating the factor of expense in the analytical method. It was shown that with a suitable shaking arrangement to ensure intimacy of contact between the hydrogen and the nickel suspension, the conversion to the hydrogenated product was rapid. Numerous examples were quoted both in the papers of Busch and Stove and of Kelber to show the accuracy of the process, and this is confirmed by a further report of Rosenmund and Zetsche[2] on numerous halogenated bodies investigated prior to 1914.

The Kjeldahl process for estimating nitrogen.—This process for estimating nitrogen in organic compounds by conversion of the nitrogen content into ammonium sulphate by digestion of the compound with concentrated sulphuric acid is normally operated with the assistance of a catalytic agent. As operated by Dyer,[3] the addition of a globule of mercury to the sulphuric acid is recommended. The mercuric sulphate thus produced acts as a promoter of the oxidation process, hastening the production of the clear, colourless liquid which must be obtained before estimation of the ammonia produced.

The Kjeldahl method is not applicable to a considerable number of organic compounds containing nitrogen, principally the nitro-derivatives and compounds having nitrogen in a ring system, as, for example, pyridine derivatives. In such cases, effort has been made to render the process applicable

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[1] *Ber.*, 1917, **50**, 305.

[2] *Ibid.*, 1918, **51**, 578.

[3] *J. Chem. Soc.*, 1895, **67**, 811.

by addition of such derivatives as the carbohydrates, sugars, and phenols, or by variation of the oxidising agent. In the latter connection, potassium permanganate, manganese dioxide, copper sulphate, phosphoric anhydride, disodium phosphate, platinic chloride, and magnesia have all been suggested as catalytic agents.

The identification and estimation of organic compounds.—The analytical operations which are involved in determining the identity and composition of organic compounds are in very great measure the application of catalytic processes. The primary operation in organic analysis is, naturally, the preparation of the substance under investigation in the highest possible degree of purity. Following this operation there arises its assignment to a definite class of compound, and, at this stage of the problem, processes of resolution into simpler or more readily identified products largely arise. Hydrolysis therefore plays a large part in such operations and the aid of catalytic agents is usual. Further, certain catalytic reactions are characteristic to definite classes of organic compounds and may be utilised in the process of identification, whilst in the determination of the individuality of a member of a given class catalytic reactions may also frequently be invoked. By a reference to the main classes of organic compounds concerned, these generalised remarks may be illustrated.

Alcohols.—Of catalytic operations in the identification of alcohols, esterification processes rank high in importance. Stephan[1] proposed the use of phthalic anhydride as a suitable acidic agent for the esterification process of identification and as a means of distinction between primary, secondary, and tertiary alcohols. Stephan found that primary alcohols reacted quantitatively to form the acid ester on being heated with the anhydride for an hour in a suitable solvent such as benzene, whereas secondary alcohols react with difficulty and tertiary alcohols not at all under the given conditions. Following the investigations of Menschutkin and others (Chapter IX), the velocity of esterification with a given alcohol under given conditions is applicable for purposes of identification.

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[1] *J. pr. Chem.*, 1899, (ii), **60**, 248.

Hell's method[1] for identification of primary alcohols of high molecular weight is, in reality, the dehydrogenation of an alcohol with simultaneous production of an acid. Soda-lime is the particular agent employed, though doubtless other catalytic agents could be used. The reaction occurring may be represented by the equation :

$$R\cdot CH_2\cdot OH + KOH = R\cdot COOK + 2H_2.$$

In the process the possibility of further decomposition of the acid according to the equation :

$$R\cdot COOK + KOH = R\cdot H + K_2CO_3,$$

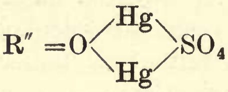
must be observed. Especially with lower primary alcohols is this reaction predominant. According to Bancroft,[2] the dehydrogenation process takes place in several stages representable by the equations :

$$CH_3\cdot CH_2\cdot OH + NaOH = CH_3\cdot CHO + NaOH + H_2O =$$
$$CH_2\cdot CO + NaOH + 2H_2 = CH_3\cdot COONa + 2H_2.$$

The caustic soda is the catalytic agent, the lime being practically inert at the temperatures of operation.

In the oxidation of alcohols, the use of catalytic agents is possible and the variation in the reaction products, aldehyde and acid from primary alcohols, ketones from secondary alcohols and ketones, and acids of lower carbon atom content from the tertiary alcohols, serves to indicate the type of alcohol under study.

The tendency of the tertiary alcohols to form ethylenic hydrocarbons permits of the application of the reaction of Denigès,[3] whereby, on heating a few drops of the alcohol with a solution of mercuric oxide in dilute sulphuric acid, a yellow or red precipitate of the characteristic compounds



is obtained.

For the phenols, the coloration test with ferric chloride is

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[1] *Ann. Chim.*, 1884, **223**, 269.

[2] *J. Physical Chem.*, 1917, **21**, 594.

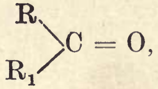
[3] *Compt. rend.*, 1898, **126**, 1277.

the most general method of identification, and consequently catalytic operations are but little employed. It may be observed, however, that in acid esterification processes the phenols, in general, do not yield esters except in those cases in which, owing to substitution in the ring, the hydroxyl group is rendered strongly negative.

Acids.—As with alcohols, esterification is largely employed in the identification of organic acids, and the general methods of catalytic acceleration as outlined in a preceding chapter are applicable. The velocity of esterification may be utilised to differentiate between primary, secondary, and tertiary acids, in which case the data compiled by Menschutkin and others on constitution influences in esterification are employed. In general, the esterification method of Fischer and Speier[1] is adopted for purposes of identification.

Anhydrides and lactones.—Processes of hydrolysis with subsequent identification of the acids produced are employed in the analysis of anhydrides and lactones. The earlier discussion of these reactions outlines the catalytic principles involved and the agencies employed for promotion of the reaction.

The carbonyl grouping.—In the identification of ketones, aldehydes, sugars, and other organic compounds containing the characteristic carbonyl grouping,



the possibility of applying catalysis is most marked. Fischer's method[2] of identification of the carbonyl grouping by conversion to the phenylhydrazine derivatives is markedly influenced by catalytic agents both positive and negative. Ordinarily, the reaction is carried out by warming the substance with phenylhydrazine hydrochloride in weak acetic acid solution, but Schottle[3] has directed attention to the negative catalytic effect of small amounts of this acid as well as of the free mineral acids such as hydrochloric, sulphuric, and especially nitrous acid. The reaction, however, occurs

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[1] *Ber.*, 1895, **28**, 1150, 3252.

[2] *Ibid.*, 1883, **16**, 661, 2241; 1884, **17**, 572.

[3] *J. d. physik-chem., Ges.*, 1911, **43**, 1190.

much more rapidly in pure acetic acid than in water, and in this solvent proceeds even at the ordinary temperature.[1] The insolubility of the hydrazones in acetic acid may account for this observation. In researches on the catalytic activity of zinc chloride, Reddellen[2] has observed the accelerating action of this compound, in the form of a phenylhydrazine complex $(C_6H_5{\cdot}NH{\cdot}NH_2)_2ZnCl_2$, on the Fischer reaction for ketones.

The corresponding reaction of the carbonyl grouping with hydroxylamine[3] whereby aldoximes and ketoximes are produced, is similarly retarded, according to Schottle[4] by the presence of mineral acids. Caustic potash or soda, on the other hand, act as accelerators.[5]

The catalytic features of the aldol condensation as applied to the identification of aldehydes has been previously considered (p. 322).

Oxidation and reduction of the carbonyl grouping with subsequent identification of the resulting products may also be employed in the determination of aldehydes and ketones, with simultaneous application of catalytic methods.

The use of alkali in promoting the iodoform reaction for acetone is a specific example of catalysis in organo-analytical practice, applicable both qualitatively and quantitatively.[6]

Carbohydrates and sugars.—The reaction of the sugars with phenylhydrazine to yield hydrazone and osazone is due to Fischer,[7] and was used by him in the identification and elucidation of the various possible isomers.

Maquenne[8] proposed to utilise the yield of the reaction to yield osazone, under definite conditions of concentration, temperature and time, as a method of identification of the various sugars. Under the prescribed conditions, it was found that the yield of hydrazone from 1 gram of sugar was greatest in the case of sorbose and least with lactose and maltose.

The Tollens reaction is principally employed in the identifi-

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[1] Overton, *Ber.*, 1893, **26**, 20.

[2] *Ann. Chim.*, 1912, **388**, 165.

[3] Meyer and Janny, *Ber.*, 1882, **15**, 1324, 1525, 2778; 1883, **16**, 170.

[4] *Loc. cit.*

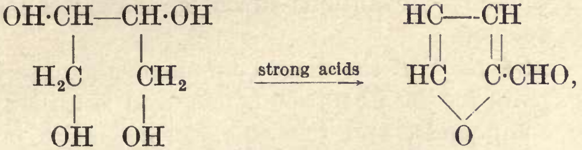
[5] Auwers, *Ber.*, 1889, **22**, 609.

[6] Lieben, *Ann. Chim.*, 1870, **7**, 236.

[7] *Ber.*, 1884, **17**, 579; 1887, **20**, 833.

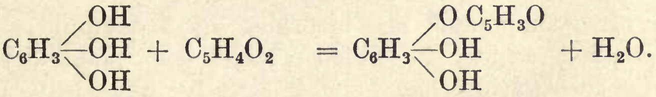
[8] *Compt. rend.*, 1891, **112**, 799.

cation of pentoses. This reaction is based upon two separate processes, (*a*) the conversion, under the influence of acids, of pentoses into furfurol,



Pentose. Furfurol.

(*b*) the condensation of the furfurol thus formed with a suitable reagent, as, for example, phloroglucinol or orcinol, to yield a characteristically coloured condensation product,



Phloroglucinol + furfurol → furfurol phloroglucide + water.

As catalytic agent for both hydrolytic split and subsequent condensation, strong hydrochloric acid is usually employed. With phloroglucinol, a cherry-red coloration is given, which subsequently changes to a dark coloured precipitate of the phloroglucide. With orcinol, a colour change from red, through violet, to a final blue green is obtained, followed by separation of a blue green precipitate. The method has been employed by Tollens, Kröber, and Rimbach[1] for the quantitative estimation of pentoses.

The identification of polysaccharides is conducted by means of hydrolysis, using accelerating agents, chiefly mineral acids, with identification of the products of the hydrolytic split.

Amines, amides, nitriles, diazo- and nitro-compounds.—In the identification and estimation of amines, catalytic methods are not normally employed.

For the qualitative and quantitative estimation of amides and nitriles, hydrolysis of the substance, followed by estimation of the ammonia formed or of the acid produced, is the usual method of procedure. Ordinarily, hydrochloric acid is employed as hydrolytic agent. For difficultly hydrolysable nitriles, Sudborough recommends the conversion of the nitrile to acid amide by digestion with 90 per cent. sulphuric acid.

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[1] *Zeitsch. angew. Chem.*, 1902, **15**, 477.

followed by conversion to the carboxyl derivative by treatment with nitrous acid. The same treatment is applicable to acid amides. Hydrolysis may also be effected in alkaline solution, whereby precautions must be taken to collect the ammonia evolved.

In the estimation of the diazo-compounds, the use of dilute acids as agents for the liberation of nitrogen is utilised for the aliphatic compounds, and the observations made previously in this reaction apply also to the quantitative estimation, in which, normally, dilute sulphuric acid is the reagent used. With the aromatic diazo-group, a 40 per cent. sulphuric acid is employed to decompose the compound, the nitrogen from which may be collected in a Lunge nitrometer.

The nitro-compounds are identified by reduction to the corresponding amine, in which process the possibility of utilising accelerating agents has already frequently been emphasised.

Halogen derivatives.—The catalytic process outlined in the section on elementary analysis was originally employed as a method of identification of halogen-substituted organic compounds and by the later investigations was shown to be quantitatively applicable.

Esters and glucosides.—Hydrolysis of these compounds with subsequent identification of the products is the normal course of procedure. Both acid and alkaline hydrolysis is utilised, according to desire, the principles involved in both being fully set forth in the chapter dealing with hydrolysis.

The proteins.—The researches of Emil Fischer on the constitution of the proteins are admirable illustrations of the application of catalysis in organic investigation. Fischer showed that, on hydrolysis, the proteins yielded a large number of amino-acids, the individual proteins differing from one another in respect of the number and quantities of the acids obtained by the hydrolytic process, using strong acids as accelerating agent. Both monobasic and dibasic amino-acids, as well as diamino-acids, have thus been isolated from the products of hydrolysis, and from a given protein as much as 70 per cent. of the theoretical yield has been obtained, in the form of different amino-acids, thus showing that the protein molecules consist essentially of conjugations of a large number of amino-acids, schematically representable by the formula :

$$\mathrm{COOH{\cdot}R{\cdot}CH{\cdot}NH - CO{\cdot}R_1{\cdot}CH{\cdot}NH{\cdot}CO{\cdot}R_2CH{\cdot}NH{\cdot}CO \ldots\ldots NH{\cdot}CO{\cdot}R_n{\cdot}CH{\cdot}NH_2.}$$

The approximately quantitative method of estimation of the hydrolysis products may be outlined. The protein is hydrolysed by means of sulphuric or hydrochloric acid, generally the latter, in the form of acid of sp. gr. 1·19. The progress of the hydrolysis is followed by means of the biuret test for protein, the production of a reddish-violet to blue coloration in presence of very dilute copper sulphate solution, and sodium hydroxide. After completion of hydrolysis, the mixture is concentrated in a vacuum and saturated with hydrogen chloride, whence on standing the hydrochloride of glutamic acid separates out. The succeeding operation is the esterification of the monoamino-acids in alcoholic solution of hydrogen chloride, several successive operations being necessary in order to overcome the hydrolytic effect of the water produced in the esterification process. The subsequent operations consist in the liberation of the free esters from their hydrochlorides and in the separation by fractional distillation, in a vacuum, of the amino-acids into various groups arranged in order of their volatility. To get more effective separation the process involves hydrolysis of the esters and a laborious process of fractional crystallisation of the amino-acids.

Physico-chemical measurements of catalysis in analytical chemistry.—To the reader who has perused the preceding chapters it must have been evident that a considerable number of the reactions which are therein discussed are readily applicable to the processes of analytical chemistry. Especially in those branches of analysis in which equilibria are present are the normal analytical operations inapplicable, since in the majority of cases these latter are conducted with displacement of the equilibria prevailing. For example, it is obvious that the ordinary analytical processes are frequently not applicable to the determination of the concentrations of hydrolytic products of a given substance in a solution, since they often consist in methods of precipitation or in general of removal of components of the system from the sphere of reaction, which obviously results in displacement of the prevailing equilibrium. In cases such as these, the application of physico-chemical methods are invaluable, as may be illustrated by the use made of them by Bredig and by Walker and his co-workers in the examples previously cited in the section on diazoacetic ester decomposition (Chapter VIII). Also, it is evident that physico-chemical methods are also widely applicable to a variety of determinations of organic substances, in which the complexity of the materials is a distinct difficulty in the way of ordinary analytical operations, but with which, by a study of their various reactions, in many of which catalytic change is involved, physico-chemical measurement becomes in the most marked degree a useful method of analysis.

The field of reactions involved in a discussion of such measurements extends into both sections of chemical analysis, inorganic and organic. It is preferable, therefore, in order to summarise the various applications of this type, to adopt a classification based upon the agent which is active in the promotion of the catalytic change, to group them therefore according to the part played by hydrogen or hydroxyl ion, water, neutral salt, or gas in promoting the reaction under consideration. In such a way the field of study may be more succinctly covered.

Water.—The *rôle* of water in various oxidation processes has long been a matter of note. Bergmann's observations that phosphorus oxidises more slowly in dry air than in moist, is but one of many early observations of the action of water graphically emphasised by Mrs. Fulhame in her "Essay on Combustion," London, 1794. The views of Mrs. Fulhame on the intervention of water in the oxidation of carbon monoxide were revived by the communication of Dixon to the British Association in 1880, to the effect that the union of carbon monoxide and oxygen only occurred in the presence of water vapour. Baker[1] extended the observations on the accelerating action of water vapour to the combination of ammonia and hydrogen chloride, as well as to the dissociation of the corresponding ammonium salt, to the combination of sulphur trioxide and lime, and to the reaction between illum-

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[1] *J. Chem. Soc.*, 1894, **65**, 611.

inated hydrogen and chlorine. Further bibliography on the influence of moisture on chemical change has also been compiled by Mellor and Russell.[1] It is evident, however, that such positive catalytic influences of water vapour are but little applicable to the purposes of analytical work. On the other hand, in a number of reactions in which water functions as a negative catalyst, analytical applications are possible.

In a preceding chapter, in the discussion of esterification processes, it was pointed out that the presence of small quantities of water exhibit extraordinary inhibitory effects on the velocity of esterification in alcoholic solutions. This observation furnished Goldschmidt with a method for the determination of small amounts of water in alcohol,[2] consisting in the determination of the velocity of esterification of a 0·1-normal solution of phenylacetic acid in solution in the given example of alcohol, using hydrogen chloride of concentration 0·1-normal as catalytic agent. By comparison of the reaction constant obtained with the alcohol under investigation with the values yielded by alcohol containing definite known amounts of water, the aqueous content of the alcohol sample could readily be deduced. A similar application of the principle to methyl alcohol is due to Gyr,[3] who employed the same concentrations of esterifiable and catalytic acid as were used by Goldschmidt.

A corresponding application of reaction velocity measurements with the analytical determination of water concentrations in alcohols was furnished by the observations of Bredig and Fraenkel[4] on the inhibitory action of water on the catalytic decomposition of diazoacetic ester in alcoholic solutions by aid of acids. It was shown that the reaction constant in presence of 0·00909-normal picric acid was as much as $k = 0{\cdot}0524$ in ethyl alcohol dried over calcium, whereas with alcohol containing 0·18 per cent. of water the constant had sunk to 0·0401. The observations of Bredig and Fraenkel were subsequently extended by Millar, to whom is due the

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[1] *J. Chem. Soc.*, 1902, **81**, 1272.

[2] Goldschmidt, with Sunde, *Ber.*, 1906, **39**, 711; with Udby, *Zeitsch. physikal. Chem.*, 1907, **60**, 728.

[3] *Ber.*, 1908, **41**, 4308.

[4] *Ibid.*, 1906, **39**, 1756.

following table of reaction constants in ethyl alcohol, dehydrated by distillation three times from metallic calcium, in presence of varying concentrations of water, employing 0·00909-normal picric acid as catalysing acid.

Water concentration in gram-mol. per litre.	k.	Water concentration in gram-mols. per litre.	k.
0·00	0·0570	0·64	0·0175
0·02	0·0534	1·28	0·0115
0·04	0·0467	2·56	0·00645
0·08	0·0424	5·12	0·00435
0·16	0·0334	10·24	0·00491
0·32	0·0256	15·24	0·00760

The table demonstrates that the reaction velocity passes through a minimum with large concentrations of water, so that the method of estimation is only applicable to small concentrations, the disturbing effect of the corresponding reaction in aqueous solutions making itself felt at higher concentrations. Millar showed that the retarding action of water increased with increasing complexity of the alcohol; thus, with methyl, ethyl, and isobutyl alcohols the retardation by 0·32 mol. of water per litre is in the ratio 37 : 55 : 72 per cent.

A further observation of the inhibitory action of water is also due to Bredig, who in co-operation with Lichty[1] demonstrated that the decomposition of oxalic acid in presence of concentrated sulphuric acid according to the equation:

$$(COOH)_2 = CO_2 + H_2O,$$

is retarded by the presence of water. It was shown that the influence of traces of water was so great that it was possible to determine, by means of reaction velocity experiments, concentrations of water which could not be detected by the ordinary analytical methods, or even by determination of the electrical conductivity. Thus, the time required to decompose a given quantity of oxalic acid at 25° rose from fifteen minutes in 100 per cent. sulphuric acid to two hundred and eighty five minutes when 0·1 per cent. of water was present. With larger concentrations of water, the rate of reaction became so slow that it was necessary to carry out the investigations at still higher temperatures. It was then found that

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[1] *Zeitsch. Elektrochem.*, 1906, **12**, 450; *J. Physical Chem.*, 1907, **11**, 225.

at 45° the concentration interval of 0·1 — 0·6 per cent. water could readily be investigated. Higher concentrations of water were investigated at a temperature of 70°. The accompanying diagrams (Fig. 33) illustrate the retarding influence of the water in such circumstances. It must be observed that the presence of sulphates in the acid is not permissible, since they also exert an inhibitory action upon the velocity of reaction.

Hydrogen ion.—Physico-chemical measurement of hydrogen-ion catalytic activity is mainly confined, in analytical chemistry, to four reactions, the inversion of sugar, the velocity of esterification, the rate of ester hydrolysis, and the decomposition of diazo-esters. Of all these reactions, the theoretical aspects have previously been discussed. Their applications to problems of analysis remain to be mentioned.

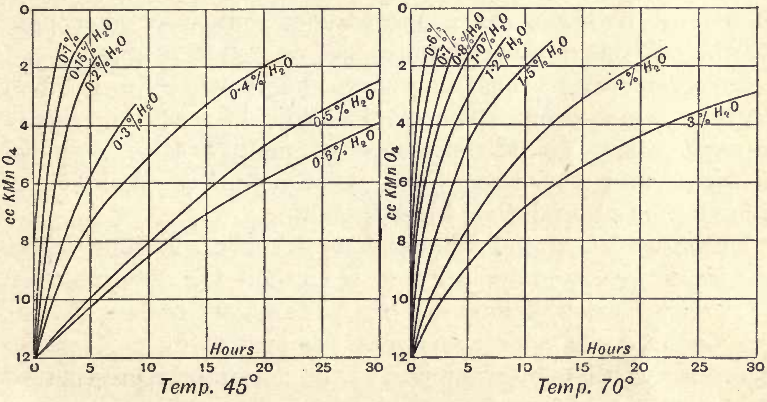

FIG. 33.

Naturally, use may be made of any of these reactions for the determination of hydrogen-ion concentration. Thus, Walker utilised the measurement of the rate of hydrolysis of esters[1] to measure the hydrolysis of salts yielding acidic products of hydrolysis, and Walker and Aston[2] utilised the inversion of cane-sugar to the same end. Walker and Wood[3] employed both these reactions to determine the hydrolysis

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[1] *Zeitsch. physikal. Chem.*, 1889, **4**, 319.

[2] *J. Amer. Chem. Soc.*, 1895, **17**, 576 ; 1897, **18**, 120, 693.

[3] *J. Chem. Soc.*, 1903, **83**, 484.

of urea hydrochloride. Walker and Cumming[1] applied the diazo-ester decomposition to the general problem of the acid concentrations of amphoteric electrolytes, whilst Spitalsky investigated, in the same manner, the hydrolysis of potassium dichromate.[2] The operations are also applicable to biological investigations as illustrated by the determination by Laborde[3] of the acidity of the gastric juice by measurement of the rate of inversion of cane-sugar. Hoffmann[4] elaborated the method of estimation, using the inversion of cane-sugar and the hydrolysis of methyl acetate.

As emphasised in the section on identification of organic compounds, determination of reaction velocity in presence of definite hydrogen-ion concentrations may also be utilised for the analysis of acids and alcohols, as well as of esters.

In regard to all such measurements, however, a word of warning is necessary. The modifications of reaction velocity brought about by the presence of neutral salts, colloidal material, and the like, limit, strictly, the applicability of this method of analytical investigation.

Measurement of the polarisation of sugar solutions before and after inversion by acids is a method for determination of sugar concentrations. With cane-sugar present alone, the operation is simple, as was demonstrated by Clerget.[5] The operation has been applied to the determination of added cane-sugar in wine and in condensed milk, in the latter case even in presence of milk-sugar, since with a 0·3 per cent. hydrochloric acid solution, which is sufficient for the inversion of the cane-sugar, the milk-sugar is not attacked. Polarimetric measurement, before and after inversion, is also employed in determination of mixtures of raffinose and cane-sugar, the former of which is inverted about 20 per cent. less rapidly than the latter. The raffinose on inversion yields a mixture of the three sugars, glucose, fructose, and galactose, which mixture has, therefore, a greater dextrorotatory power than ordinary invert-sugar.

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[1] *Zeitsch. physikal. Chem.*, 1907, **57**, 578.

[2] *Zeitsch. anorg. Chem.*, 1907, **54**, 265.

[3] *Gaz. méd.*, Paris, 1874, **9**.

[4] *Zentralbl. klin. Medicin*, 1889, **10**, 793; 1891, **11**, 521; *Zeitsch. anal. Chem. Ref.*, 1891, **30**, 392

[5] *Ann. Chim. Phys.*, 1849, (iii), **26**, 175.

Hydroxyl ions.—Of reactions adapted to the determination of hydroxyl-ion concentration, those based on the catalytic influence of alkalis on change of optical rotation are, from the historical point of view, the first to be discussed. Urech[1] showed the dependence, on the strength and concentration of various bases, of the mutarotation of milk-sugar, but the operation of a catalytic influence in this case was first pointed out by Ostwald. Consequently, Bredig[2] cites the investigation of Will and Bredig[3] on the action of bases on optical rotatory power in the conversion of hyoscyamine to atropine as the first example of hydroxyl-ion catalysis, with which, moreover, the ion concentration may conveniently be measured as well as by means of the corresponding racemisation of scopolamine.[4] The reaction occurring is monomolecular and proportional to the hydroxyl-ion concentration, the bases being active in the order of their electrical conductivity. Instances of such measurements could be multiplied, and include the racemisation of tartaric acid,[5] of cotarnine by Dobbie, Lauder, and Tinckler,[6] of amygdalin[7] and of mandelic acid by McKenzie and Thompson.[8] According to researches of Trey[9] and Osaka,[10] the most accurate method of measuring hydroxyl-ion concentration is in the change of optical rotation of *d*-glucose.

The utility of alkalis in promoting the aldol condensation as outlined in the chapter on organic synthesis is also illustrated in the investigations of Koelichen,[11] who showed that the condensation of acetone to diacetone alcohol,

$$2CH_3\cdot CO\cdot CH_3 \rightarrow CH_3\cdot CO\cdot CH_2\cdot C(OH)\cdot(CH_3)_2,$$

as well as the decomposition of the latter, was promoted by the addition of alkali, and that, as proportionality existed between hydroxyl-ion concentrations and reaction velocity,

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[1] *Ber.*, 1882, **15**, 2130 ; 1883, **16**, 2270 ; 1885, **18**, 3059.

[2] "Altes u. Neues von der Catalyse," *Biochem. Zeitsch.*, 1907, **6**, 283.

[3] *Ber.*, 1888, **21**, 2777.

[4] Herz, *Chem. Zentr.*, 1911, **15**, 67.

[5] Holleman and Böeseken, *Rec. Pays-Bas*, 1897, **17**, 66 ; Winther, *Zeitsch. physikal. Chem.*, 1906, **56**, 465, 719.

[6] *J. Chem. Soc.*, 1903, **83**, 472 ; 1904, **85**, 121.

[7] Walker, *ibid.*, 1903, **83**, 472.

[8] *Ibid.*, 1905, **87**, 1019.

[9] *Zeitsch. physikal. Chem.*, 1895, **18**, 193 ; 1897, **22**, 424.

[10] *Ibid.*, 1900, **35**, 661.

[11] *Ibid.*, 1900, **33**, 149.

the change could be employed as a measure of the ionic concentration. The volume change accompanying the reaction was used to determine the reaction velocity, the system under investigation being contained in a dilatometer. The reversibility of the process was particularly well investigated, it being demonstrated that the equilibrium position was unchanged by the presence of the catalyst, and independent of its nature.

In the saponification of esters, also, a convenient method

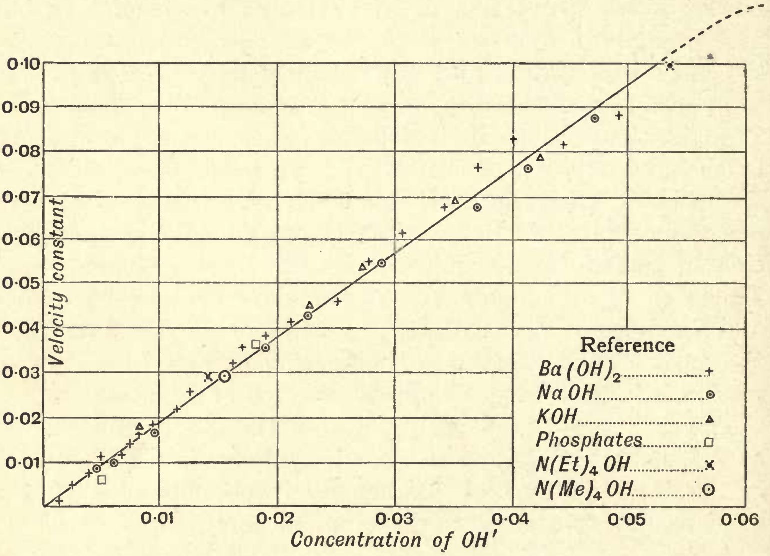
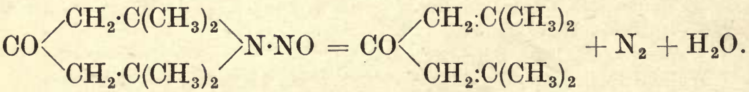


FIG. 34.

of determining hydroxyl-ion concentration is evidently available.

A recently investigated example of catalytic activity of hydroxyl ions is the decomposition of nitrosotriacetonamine, by alkalis, into phorone and nitrogen as represented by the equation :



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{CH_2\cdot C(CH_3)_2}\\ \mathrm{CH_2\cdot C(CH_3)_2}\end{matrix}\right\rangle\mathrm{N\cdot NO} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{CH_2:C(CH_3)_2}\\ \mathrm{CH_2:C(CH_3)_2}\end{matrix}\right. + \mathrm{N_2} + \mathrm{H_2O}.$$

It was shown by Francis and Clibbens,[1] and by Francis and

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[1] *J. Chem. Soc.*, 1912, **101**, 2358.

Geake,[1] that the monomolecular reaction, occurring in presence of alkalis, was available for the estimation of the concentration of the hydroxyl ions up to the value 0·05 normal. Beyond this concentration and up to 0·3*N*-hydroxyl ion the unimolecular constants showed a drift rendering the method inapplicable for determination of ion concentration in this interval, above which, however, results were again obtained from which ion concentration could be deduced. The accompanying diagrams (Figs. 34 and 35) illustrate the results obtained. The reaction was very conveniently investigated, in the manner employed in the studies of acid catalysis in the diazoacetic ester decomposition, by observation of the nitrogen evolved.

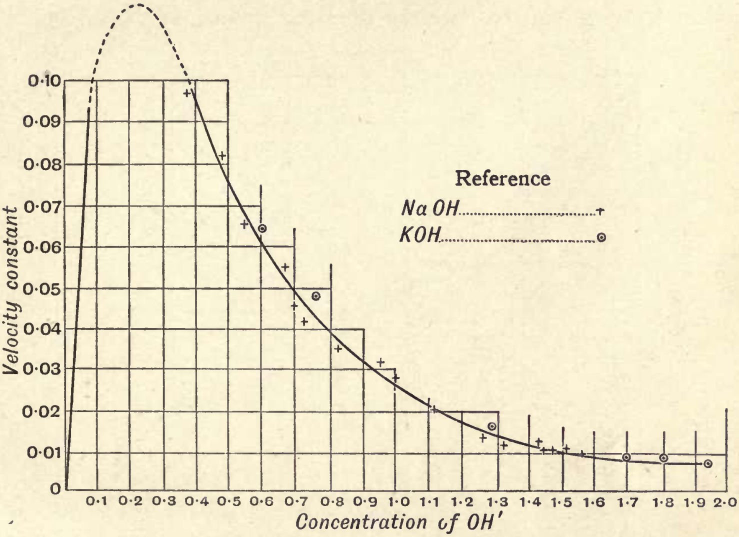

FIG. 35.

The effect of neutral salts on the velocity constant of the decomposition of nitrosotriacetonamine when the concentrations of hydroxyl ions are small[2] is shown in the accompanying diagram (Fig. 36) where the percentage retardations are plotted against the concentration of the neutral salts used. It follows, therefore, that when this method for the deter-

[1] *J. Chem. Soc.*, 1913, **103**, 1722.

[2] *Ibid.*, 1915, **107**, 1651

mination of alkalinity is used, due allowance must be made in the value of the velocity constant found if neutral salts be present, and the method may thus lose some of its convenience as a method of estimation.

The method has also been applied to a number of other nitrosoamines with similar results, typical examples of which are included in the plot of results given in Fig. 37 (p. 479).

Salts as catalytic agents.—The anions of a number of salts have been shown to function catalytically, and in illustration thereof the researches of Bredig and Walton[1] on the activity of iodides in the decomposition of hydrogen peroxide, and of Bredig and Stern[2] on the influence of cyanides in the condensation of benzaldehyde to benzoin may be cited.

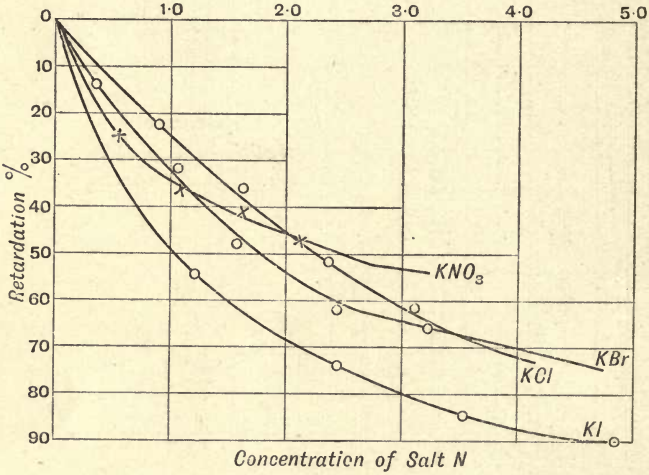

FIG. 36.

Walton showed that the decomposition of the peroxide in presence of potassium, sodium, and ammonium iodides was a reaction of the first order, the velocity of which was proportional to the concentration of iodide ion. With cadmium iodide, which, as is well known, forms a complex anion, the ratio of reaction velocity to concentration of iodide was considerably reduced. Also, the formation of anion complexes with potassium iodide, as, for example, by addition

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[1] *Zeitsch. physikal. Chem.*, 1904, **47**, 185.

[2] *Ibid.*, 1905, **50**, 513.

of iodine or mercuric iodide, similarly resulted in a diminution of reaction velocity.

In the cyanide reaction, Stern showed that the reaction velocity was the same in equal cyanide-ion concentrations, whether from sodium, potassium, or barium cyanides, completely analogous therefore to the behaviour of the hydroxides in the saponification of esters. Complex cyanide formation, also, lowered the reaction velocity, confirming, therefore, the view of anion activity.

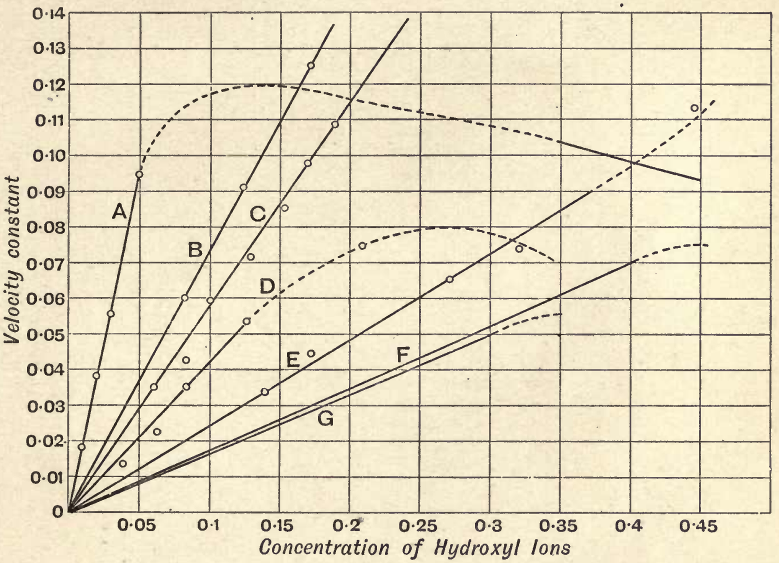

FIG. 37.

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