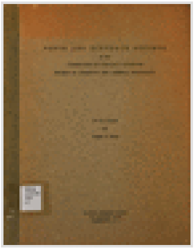

Tenth and Eleventh Reports of the Committee on Contact Catalysis, Division of Chemistry and Chemical Technology (1935)

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TENTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS

Guy B. Taylor

(Contribution No. 124 from Experimental Station,
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The members of the Committee on Contact Catalysis are: Wilder D. Bancroft, Chairman, Homer Adkins, E. Frankland Armstrong, R. E. Burk, J. C. W. Frazer, J. Newton Pearce, E. Emmet Reid, Guy B. Taylor, H. S. Taylor.

1935

The great generalization in the field of contact catalysis is yet to be formulated. Catalysis is concerned with reaction speeds and with the course of events intervening between the bringing of reactants together and the withdrawal of the final reaction products. Predictions of activity are still virtually impossible. There is no generalization at all comparable in importance or usefulness to the structural formula of the organic chemist, the phase rule of the physical chemist or thermodynamics. Take one simple illustration. The structural formula tells us what ethanol is, that removal of water yields ethylene, that removal of hydrogen yields aldehyde. Thermodynamics predicts precisely the temperature and pressure favorable to either dehydration or dehydrogenation. Neither reaction will run spontaneously. The catalyst necessary for promoting the reactions can not be predicted.

Tolman (1), in his book, "Statistical Mechanics", says: "The problem of reaction velocities is probably nearer to the heart of most chemists than anything else in their whole range of activity. Rates of reaction are the factors that determine yields, and costs, and possibilities, and their theory must eventually succumb to scientific treatment ----- but the field still remains one of the most obscure in chemistry. - Whatever may be, the way is long and the traveller must not tarry."

Downs (2) strikes a similar note: "There is no royal road to learning, nor a library-chair route to the catalytic reaction. Physical chemistry in the athletic rather than the Spencerian definition is required; more hard labor in the laboratory rather than pen pushing with a flourish; more statement of fact with less verbose conclusions based on a few experiments. --- We maintain that empiricism still prevails, and will until we have accumulated much more information than is now available. At that time, and to a small degree now, we may allow ourselves to predict the probable course of reaction and the conditions required because of this background in the art. The test of any theory must reside in a prediction and a fulfillment."

H. S. Taylor (3), while recognizing the situation, is more optimistic: "The application of the term 'catalysis' to a set of chemical phenomena is, in major part, a confession of ignorance. It normally indicates the existence of a series of chemical reactions of which the initial and final states are readily stated, while, of the path between, little or nothing is yet known. When known, the need for the term 'catalysis' disappears, for the total process becomes a succession of normal chemical reactions. This is true alike of the so-called catalytic reactions in homogeneous systems and of the heterogeneous catalytic reactions, those occurring at surfaces. The use of the term 'catalysis' will steadily yield to a more penetrating analysis of the detailed steps of the gross process."

The last two reports (4) of the Committee on Contact Catalysis were rather comprehensive reviews of the state of the art. These papers cover theory and practice through 1930 and tie in prior work so well that the present writer has deemed it sufficient in compiling this Tenth Report to cover only items actually published in 1931. The actual number of novel ideas published in 1931 was relatively small. Explanations of specific catalytic reactions were largely stated in terms of theories older than the year.

Current theories still center largely around processes called adsorption. Experimentally, adsorption is measured by the disappearance of gases when brought into contact with solid surfaces. It is generally held these days that the gas is spread on the surface as a monomolecular film. Early attempts to correlate quantity adsorbed and catalytic activity were not successful. The fact that traces of catalytic poisons could not possibly cover the entire surface was a major factor in the development of the idea that only a fraction of the total surface is catalytically active. Attempts to correlate the measured energetics of adsorption with activity have not been particularly fruitful.

The latest development in adsorption theory postulates more than one kind of adsorption. The genesis of this idea arose from the work of Benton and White (5), who found discontinuities in adsorption isotherms on catalysts when measured below 0°C. Allmand and Burrage (6) report the same phenomena with vapors on charcoal. Benton argues that step-wise curves are obtained for physical adsorption, that the molecules go on the surface in rows and possess mobility on the surface. At higher temperatures the adsorption is partly chemical, activating the adsorbed gas.

A definite theory that the kind of adsorption important in catalysis requires an activation energy has been put forward by H. S. Taylor (7). The experimental evidence rests largely on the fact that in many cases adsorption is not instantaneous, and that values can be calculated for heats of activation from temperature coefficients by the familiar equation

$$d \ln k/dT = E/RT^2$$

This theory has been criticised by Steacie (8), who points out that solubility of gases, especially in metals, may be the actual slow process involved and not adsorption. Ward (9) takes the same view. Müller and Schwabe (10) also support the solubility idea in their work with hydrogen and metals of the platinum group.

Since the entire subject of adsorption has been adequately and thoroughly discussed by the leaders in the field in the Transactions of the Faraday Society (March and April 1932), it need not be elaborated here. The preponderance of the evidence certainly points to more than one kind of adsorption for certain gas-solid systems. To anyone who has observed the effect of removing a bath of liquid air or solid carbon dioxide surrounding a tube of nickel catalyst during an adsorption measurement, it would be difficult to believe otherwise. In such a case the writer has seen the pressure of hydrogen rise from a few millimeters to above an atmosphere in a few minutes and then fall in a second or two to less than 0.01 mm.

The siguation regarding adsorption may be summerized by saying that there are four possibilities. First, the gas may be held strictly by molecular or van der Waals' forces; in this case the process is relatively rapid, involves a low heat of adsorption, is easily reversible and occurs at low temperature. Second, chemical or specific adsorption is slower but reversible, occurs at higher temperatures and with higher heats of adsorption. It requires an energy of activation. The third is a type of chemical adsorption that is not reversible (e.g., oxygen on platinum or on charcoal). The fourth is solution in which the gas actually penetrates into the body of the solid. Experimentally it is not easy to separate the four possibilities since all types may occur simultaneously. It is not surprising, then, that differences of interpretation exist.

The evidence that the second type of adsorption controls the contact catalytic reaction has been furnished chiefly by H. S. Taylor and his students at Princeton. Palladium shows a rise in adsorption capacity for carbon monoxide from 195°K. to 273°K. (11). Manganous oxide and manganous-chromic oxide, which are hydrogenation catalysts, adsorb hydrogen slowly at high temperatures (say above 184°C.) and much more than at room temperature (12). Zinc oxide exhibits activated adsorption for hydrogen from 0°C. upward (13). Garner and Kingman (14) have furnished data along the same lines for oxide catalysts, and heats of adsorption as well, for both carbon monoxide and hydrogen. Now while all these cases do demonstrate a slow adsorption at temperatures where the catalysts are normally active, and to such adsorption activation energy can logically be ascribed, the only attempt so far recorded to make a prediction on the basis of the energy activation theory has been only partly successful. Williamson and Taylor (15) studied the decomposition of alcohols on oxide catalysts and ventured the prediction that surfaces mainly dehydrogenating must activate hydrogen at a lower temperature than water vapor. In an actual attempt to demonstrate this effect on zinc oxide, Taylor and Sickman (16) found that water vapor did not meet the criterion for activated adsorption in one way but did in another. Water vapor was adsorbed almost instantly at room temperature, but the expected rise and subsequent fall of pressure on heating was not observed. On the other hand a slow adsorption of water vapor did occur at 270^{o}C. on the catalyst already having some water on its surface.

The ortho-para hydrogen interconversion must involve activating the hydrogen according to H. S. Taylor (17) and this phenomenon has been worked into his theory of activated adsorption.

In the field of experimentally determined energetics of adsorption, the evidence for a peak in the curve of mass of gas adsorbed versus calories is steadily diminishing (9)(14)(18), although H. S. Taylor (7) has presented a plausible reason for a peak in special cases. The surface varies in activity and the energy of activation increases with the surface covered. This energy may rise enough to offset steadily falling values of the heat of adsorption.

No generally acceptable theory has yet appeared to explain specificity of catalysts. In many cases, where two or more reactions are possible, all will take place to some extent. In other cases one of the reactions may be largely suppressed merely by variation of the method of preparation of the catalyst. Bancroft and George (19) report such an instance in the decomposition of ethyl acetate on alumina. A case of very marked selectivity in hydrogenation is that of the difficultly reducible oxides. Vaughen and Lazier (20) show that these oxides will not effect the hydrogenation of ethylene or any alkene but are quite effective in the hydrogenation of acetone. Their capacity for alcohol synthesis, by causing the reaction of hydrogen and carbon monoxide, is well known. Explanations of what may be called the chemical nature of surfaces continue to revolve around unsaturated atoms in the crystal lattice, polar bonds, specific ion effects and things of similar character. A new variation of such explanations may be cited in Westling's suggestion (21) that metals catalyze reactants with like atomic spacing to their own. Born and Weisskopf (22), in a mathematical treatment, attempt to correlate reaction rate in adsorption catalysis with atomic distance and vibrational quantum number.

The physical conception of what happens on a catalytic surface has not changed much during the period under review. Schwab and Rudolph (23) present further evidence to support their theory that the seat of activity resides on edges and corners of crystals. Belief in the movement of adsorbed reactants over the surface is increasing (24). This is sometimes called lateral diffusion. That something more is needed to secure high activity than mere extent of surface is indicated by the work of Gibbs and Liander (25) with nickel aerosol, and of Hüttig, Kostelitz and Fehér (26) on different particle sizes of zinc oxide in decomposing methanol.

Explanations of catalysis involving the electron continue to appear. Nyrop (27) says the catalytic effect of a surface depends on the maximum kinetic energy of "free" electrons. If the ionization energy of a molecule close to the surface is lower than the kinetic energy of some of the surface electrons, ionization occurs, and the molecule will be adsorbed in a condition where it is able to react. Poisoning of a catalyst is explained by this theory as the preferential adsorption of a product with low ionization energy. Promoters act by preserving the accessible area. Nyrop's article is a discussion and contains no experimental material. Kobozev and Anochin (28) have made an experimental study of the energy levels of adsorbed hydrogen and oxygen on metal surfaces. They find from desorption voltage curves of hydrogen on platinum 9, 11 and 13.5 volts and come to the conclusion that hydrogen can be bound to the surface with 9, 53 and 113 calories of energy, indicating three different kinds of adsorption. Oxygen gave 7, 10 and 12.5 volts. This work also puts the electron in the catalytic picture. Finch and Stimson (29) have reported further results in continuing their series of papers on the electrical condition of hot surfaces during adsorption of gases. The electric charge developed on a conductor is attributed to gaseous ions emitted by the extralattice atoms of the surface.

The number of kinetic studies published during 1931 was less than usual. In the range of low pressures measured in microns, Van Praagh and Topley (30) and Tanner and Taylor (31) have investigated reactions on hot platinum wires. The phenomena observed in both investigations had several points in common. The activity of the wire was scarcely reproducible and depended on its prior heat treatment. Activity tended to increase with use in spite of the actual minute mass of reactants involved in the wire's catalytic history. In certain cases in both investigations an induction period occurred, followed by rapid reaction, but the reaction stopped short of completion. Van Praagh and Topley studied the decomposition of nitrous oxide and Tanner the union of hydrogen and oxygen. In the latter case hydrogen peroxide as well as water was formed. The rate of the reaction varied more as a function of the temperature <u>difference</u> between the wall and the wire, than of the actual temperature of the wire itself (32). Heating the wire at 900° induced a temporary superactivation capable of causing reaction at -120°, probably the lowest temperature at which any contact catalytic reaction has been realized.

H. A. Taylor and Schwartz (33) conclude that ethyl ether is decomposed by homogeneous reaction in the presence of heated platinum or tungsten filaments. Some reactions start on a surface and spread into the gas phase by the chain mechanism. Cases in point are hydrogen and oxygen on glass, discussed by Alyea (34), and acetylene and oxygen, discussed by Spence (35). There has been, however, no general tendency to explain reactions, formally classed as catalytic, by reaction elsewhere than directly on the surface.

Dixon (36) found the rate of decomposition of ammonia on platinum to vary directly as the ammonia and inversely as the hydrogen pressure.

G. B. Taylor and Lenher (37) measured the rates of the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, from both sides of the equilibrium position. Attempts to treat the data from the standpoint of simultaneous equations failed but empirical laws for the separate reactions were obtained. The rate of formation of SO_3 is proportional to the distance to equilibrium and is retarded by oxygen proportional to the square root of its concentration. The dissociation of SO_3 is unretarded and is proportional to the distance to equilibrium. This is one of the very few published kinetic studies of a reversible reaction. Baur (38) has used the data of Taylor and Lenher to support a theory that the quotient of the velocity coefficients of the opposing reactions is equal to the equilibrium constant. His definitions of velocity constants in this case appear to be different from the classical ones.

Benton (39) has shown how to adapt the classical equations for reaction velocities developed for constant volume to flow systems at constant pressure.

No attempt will be made in this report to cover all papers published on reactions in which a contact catalyst was used. In many of these, of course, catalysts were used as a necessity or convenience to secure a particular product and the authors were little concerned with the properties of the catalyst. Brief resumés of a few representative papers in three fields are given below.

Ammonia Synthesis. Phase rule studies of the iron-nitrogen system have been made (40). Brewer (41) finds that photo-electric emissivities of alumina-promoted iron catalysts are characteristic of pure iron, but this is not true when K_2O is added. Messner and Frankenburger (42) report that tungsten adsorbs hydrogen and ammonia in a normal manner but that nitrogen forms a surface compound. Mittash and Keunecke (43) have made a detailed study of binary mixtures of molybdenum and other metals.

Hydrogenation. Nickel seems to hold its place as the prime catalyst for liquid-phase hydrogenations. Kailan and Hardt (44) report results for a number of esters and acids. Adkins, with his students, (45) gives results on a number of reactions at pressures up to 350 atms., and discusses methods of comparing activities of catalysts (46). Glass and Kahlenberg (47) studied a wide variety of supports for nickel catalysts and found some helpful and others the reverse. In the hydrogenation of phenol, the intermediate product is cyclohexanol and not benzene, according to Roberti (48). References to hydrogenation of the vegetable and animal oils with nickel are quite numerous.

Other catalysts than nickel are assuming some importance, mainly because of their selectivity (20). The difficultly reducible oxides, of the same general character as those used in methanol synthesis, can be used for certain hydrogenations. Alcohols were produced from a number of esters with a copper-chromite catalyst by Adkins and Folkers (49). Nussbaum and Frohlich (50) studied ZnO-CuO as a catalyst for methanol synthesis.

In industry the two big fields that are opening up for hydrogenation are coal and petroleum-oil. The patent literature is too large to attempt to cover it in this paper. Representative articles are those by Rogers (51) on coal and by McKee and Szayna (52) on oil.

Oxidation. Mixed oxide catalysts for the oxidation of carbon monoxide have been studied by Frazer (53) and by Neumann (54). Seuseman and Stubbs (55) converted cymene to toluic acid over vanadium oxide. Adkins and Peterson (56) got an excellent yield of formaldehyde from methanol with mixtures of molybdenum and iron oxides. The iron oxide alone was poor.

Webb (57) gives some data on spaced platinum gauzes in the oxidation of ammonia. Yee and Emmett (58) confirm the fact that hydrogen sulfide is not a poison for this reaction, while phosphine is. Taylor, Chilton, and Handforth (59) have described the commercial development of the process operating under pressure.

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In concluding this report a few remarks from the viewpoint of the applied-catalyst investigator may be worth while. The technical worker usually is first concerned with the equilibrium position of a given reaction. For any given product from specified reactants he wants to know what pressures and temperatures are favorable. There was once some debate as to whether a catalyst could shift an equilibrium (60), but such a view is hardly tenable today. If the equilibrium constants have or can be measured with any catalyst, the same constants apply to all other catalysts for that particular reaction. If the constants have not been experimentally determined, then the investigator searches for free energy data with which to compute them. If these data are lacking, he relies on the famous Nernst approximation formula.

The next step is to find an effective catalyst. This is much more an art than a science. As yet, activity cannot be predicted from any physical or chemical property, or any correlative experimental measurement. Choices for investigation are made from experience and by analogy, and then tested by running the actual reaction. Then follows the long battle of improving the catalyst, increasing its life, suppressing side reactions and the like. Catalysts, by definition, are not consumed by the reaction but none last forever. In many modern applications catalyst renewal is a major item of the cost of the product.

The field of usefulness of the catalytic reaction has been vastly expanded in the last ten years by the discoveries of syntheses starting with carbon monoxide and hydrogen as the primary raw materials. Interesting possibilities are opened up in the field of aliphatic derivatives so long dominated by the more easily reacted aromatics. Even today compounds that were once chemical curiosities can be made cheaply by the ton. The problem of developing uses for such compounds is in reality more pressing than devising methods for their manufacture, and it is this factor of use that will largely determine the rate of growth of industry in this field.

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ELEVENTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS

Robert E. Burk

(Contribution from the Morley Chemical Laboratory
of Western Reserve University)

The members of the Committee on Contact Catalysis are: Wilder D. Bancroft, Chairman, E. Frankland Armstrong, Robert E. Burk, J. C. W. Frazer, J. N. Pearce, E. Emmet Reid, Guy B. Taylor, H. S. Taylor and H. B. Weiser.

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Introduction

The practical importance of an adequate understanding of catalysis, e.g., in the fields of industry and medicine, is so great and the recent development of the theoretical fields upon which such a comprehension must depend has been so extensive and so interesting that an effort to describe the state of knowledge of the subject in the compass of a brief report is a challenge which each year becomes more fascinating as the objectives seem to come closer. Catalysis has become a sort of philosopher's stone, which, however, instead of becoming more elusive with increase in knowledge becomes less so.

Catalysis is of interest to scientists in pure and applied fields. Yet theoretical chemistry, through which we are supposed to understand it, has become involved in mathematics to a degree which renders a paper on chemical mechanism -- which is interpreted in the light of the new physics -- substantially incomprehensible to the average industrial chemist who may be interested in catalysis. Under the leadership of the new physics, theoretical chemistry appears in fact to be drifting far away from the myriad problems which objective research in industry turns up. Since the two fields are mutually dependent, it seems desirable to prevent unnecessary widening of this gap.

As applied to catalysis, therefore, this has been made an objective of this report. An attempt is also made to concentrate attention upon the particular resistance points which seem to stand in the way of progress in the subject, in addition to summarizing recent accomplishments. These desires involve too much for one man to accomplish in an expert fashion in a reasonable time.

Consequently, in addition to the members of this committee, specialists on various theoretical points have been consulted in organizing this report. They are: A. K. Brewer, J. N. Brönsted, H. von Euler, W. Frankenburger, C. N. Hinshelwood, L. S. Kassel, I. Langmuir, R. S. Mulliken, M. Polányi, G. M. Schwab, H. S. Taylor, G. W. Wheland, and C. Zener. An extremely gratifying response has been obtained from these workers. Some of them have spent a substantial amount of their time in summarizing their views as will be evident in the portions of this report where their work is reproduced.

An attempt has likewise been made to present in a brief way an up-to-date and balanced picture of the status of applied catalysis and the unsolved theoretical problems which workers in that field would like to see solved. For their assistance in this effort, the writer wishes to express his thanks to E. K. Bolton, G. Calingaert, G. Du Bois, Frank Howard, H. P. Lankelma, A. S. Richardson, J. E. Taylor, and W. R. Veazey.

CHAPTER I. THEORETICAL

General Considerations.

The subject of catalysis must be treated as a subhead under the general subject of reaction velocity. During the past fifteen years our understanding of the factors governing reaction velocities has developed rapidly, thanks to the application of kinetic theory. A substantial assimilation of this development does not require an extraordinary mind nor a mathematical training beyond that which forms a part of the training of the average graduate chemist. On the other hand, the subject appears to be experiencing further growth due to the light which the new quantum mechanics is shedding upon it and here unfortunately the "average" chemist is likely not to try to unravel the numerous and complicated equations which form the medium of expression in that subject, especially when he learns that they are "confluent hypergeometric" equations or some other unfamiliar type.

On the other hand, almost anyone interested in the subject can read with profit Arthur Haas, "Materiewellen und Quantenmechanik" (Leipzig, Akademische Verlagsgesellschaft 1930) as an introduction to the quantum mechanics.

The writer also esteems for this purpose the introduction to the third edition of Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems" (Oxford University Press, 1933). This work also serves as a proper basis for understanding much of the subject matter with which the report deals. The new chapter on homogeneous catalysis forms a good beginning in a field, the ignorance of which stands in the way of our understanding of catalysis. The broadening of the scope of this book does not seem to have diminished Hinshelwood's sense of values which has characterized previous editions. Such items in the book as the present writer would weigh somewhat differently are treated in the appropriate places in this report. This book will be referred to merely by "Kinetics". Other new books dealing with the subject matter of this report may be mentioned at this point.

G. M. Schwab's book, "Katalyse vom Standpunkt der Chemischen Kinetik", (Berlin, Julius Springer, 1931) is written from the same point of view as that of Hinshelwood which in its earlier editions, of course, precedes Schwab. The latter, however, covers more work in catalysis than does Hinshelwood. Schwab devotes a substantial portion of his book to catalysis in aqueous solutions, a subject largely omitted by Hinshelwood. This work will be referred to merely by "Katalyse".

E. von Euler and A. Ölander have written a small work entitled "Homogene Katalyse". This work lays still greater relative emphasis upon reactions in solution with fairly detailed consideration of certain reactions rather than generalities. The reactions are the inversion of cane sugar, the mutarotation of glucose, the hydrolysis and formation of carboxylic esters, the formation and equilibrium of acetanilide, the hydrolysis of dioxypiperazine, the decomposition of camphocarboxylic acid, acetoacetic ester and nitramide, the oxidation of hydroquinone, the Canizzaro reaction and the decomposition of hydrogen peroxide.

L. F. Marek and Dorothy A. Hahn in their book "Catalytic Oxidation of Organic Compounds in the Vapor Phase" (New York, Chemical Catalog Company, 1932) have collected a large amount of material on that basically important and little understood reaction - oxidation. Evidently they have read a large number of patents on the subject which speaks well for their endurance. The scope of this work (containing 472 pages) extends rather beyond the implications of the title. Thus, e.g., the hydration of olefines and the oxidation of higher molecular weight hydrocarbons are discussed. Considerable attention is given to the oxidation of petroleum and constituents thereof. This is a vast field for applied research. This book is reviewed by H. G. Beatty (1).

E. B. Maxted has produced a work of 519 pages entitled "Catalysis and its Industrial Applications" (London, J. and A. Churchill, 1933). The first two hundred pages are devoted to a theoretical discussion and of this one-fourth is devoted to adsorption. The writer is unable to recommend this portion of the book as a well-balanced review of current catalytic theory, and the only new idea which he observed, he believes to be wrong in general. This idea is that the energy of adsorption which is "transitorily free" supplies the energy of activation of the adsorption complex. On the other hand this book is of decided practical value. Thus the writer is reliably informed that the quality of the information in the chapter on the "Hydrogenation (addition of hydrogen) of Oils" is high. Maxted evidently is experienced in this and other fields of applied catalysis. The book contains a chapter on preparation of the commoner catalysts which should be very valuable. An unusually extensive discussion of catalytic poisons is also included.

M. Frankel's Katalytischorganische Arbeitsmethoden, Abt. I, Chemische Methoden, Teil 12, Hefte 1-3 of Abderhalden's "Handbuch der biologischen Arbeitsmethoden" (Berlin, Urban and Schwarzenberg, 1932), appears to be a careful and comprehensive collection of material relevant to the subject matter of the title. The work is favorably reviewed by Roger Adams (2).

M. Kröger's "Grenzflächen-Katalyse" (Leipzig, S. Hirzel, 1933) has not been reviewed by the writer. It is, however, reviewed by H. S. Taylor (3).

H. S. Taylor in J. H. Perry's "Chemical Engineer's Handbook" (New York, McGraw-Hill Company, 1934), presents a very condensed table of the various technical applications of catalysis and the catalysts which he thinks are used in them.

Moelwyn-Hughes' "Kinetics of Reactions in Solution" (Oxford University Press, 1933), attempts to take over into the field of reactions in solution the kinetic methods which have been found successful in gaseous systems. He has performed a useful service in organizing a large amount of work in this field and has made rather more progress with his objective than one might have expected. The book makes a good companion volume to Hinshelwood's Kinetics. They emanate from the same laboratory and with a common spirit. There is some overlapping but scarcely more than would be required even if the two volumes were one. Such points in the book as the writer would criticize adversely are treated in the body of this report. This book will be referred to merely by "Moelwyn-Hughes".

In the field of adsorption upon which heterogeneous catalysis is dependent, the thoughts of a number of workers were collected in a symposium held in Oxford in 1932 and published in the Transactions of the Faraday Society 28: 129 (1932). A considerable amount of attention was paid in these papers to "activated" adsorption which is discussed later in this report.

I. Langmuir's Nobel Prize address (Stockholm, December, 1932) is devoted largely to adsorption. While Langmuir states that the paper is devoted primarily to his own work and makes no attempt to cover that of others, it is a tribute to the accomplishments of Langmuir that this paper does not lack much of being an adequate review of the real progress which has been made in the understanding of this phenomenon in the last twenty years.

Dohse and Mark have recently published "Die Adsorption von Gasen und Dämpfen an festen Körpern" (Leipzig, Akademische Verlagsgesellschaft, 1933). This work is reviewed by A. S. Coolidge (4).

Kinetic Theory*

The kinetic theory of reaction velocity may be summarized by the statement that reaction velocities for "simple" reactions may be represented by the equation

$$\text{Velocity} = \underline{f}\ (\underline{c})\ \chi\ \underline{e}^{-\underline{E}/\underline{RT}}, \tag{I}$$

where $\underline{f}$ ($\underline{c}$) is a function of the concentration of reactants which, for a single homogeneous uncatalyzed reaction going to completion, is equal to that concentration, to the square of it, to the cube of it, or to the product of two or possibly three concentrations.

When more than one reaction is occurring between reactants, or between the apparent reactants and some other bodies (which case may be considered to include "material" chain reactions), or when the reverse reaction is prominent, the details of the complex mechanism may be taken into account appropriately if equation (I) is applied to each reaction which is occurring, and the overall rate evolved from those of the separate reactions.

Proceeding in this way, rate equations sometimes become complex. From the difficulty which has been experienced in evolving a universally satisfac-

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*In writing this section the author has consulted Dr. Louis S. Kassel: Paragraphs 2, page 27, 3 page 28, 1 page 33, and 3 page 34, have been substantially revised in accordance with his suggestions.

tory kinetic mechanism for such apparently simple but really complex reactions as

$$H_2 + Cl_2 = 2\,HCl$$

$$\text{and } 2\,H_2 + O_2 = 2\,H_2O\,,$$

one is inclined to regard with considerable reserve those mechanisms which have been suggested for still more complex cases, such as the photochemistry of phosgene and the oxidation of hydrocarbons, without, however, disparaging attempts to unravel such mechanisms.

In some catalytic reactions too we have more than one chemical process occurring, especially if adsorption is treated as a chemical reaction, and we may then proceed by applying equation (I) to the individual processes. This procedure has led to considerable success in interpreting the mechanisms of some heterogeneous reactions (5).

Whatever may be said for these more complex cases, there is no responsible opposition to the results of applying equation (I) to single simple reactions, as many have turned out to be, and especially are we confident that the factors contributing to reaction velocity in such cases are all expressed in the formula.

The term $\underline{E}$ is the energy of activation which has been defined in various ways (6). It will perhaps make for clarity of physical concepts without substantial disagreement with equation (I) to consider it to be energy which must be concentrated in the reacting bond or bond's in order for reaction to occur. The reduction of $\underline{E}$ constitutes the outstanding opportunity for catalysts to accelerate reactions.

The term χ represents all other factors which affect the reaction rates of molecules, including collision rates and factors representing orientation, energy transfer and reaction probabilities. In the case of unimolecular reactions (7) χ is independent of temperature and in this case may be simply a vibration frequency within the molecule (8) and perhaps the vibration frequency of the bond which breaks. The latter idea is equivalent (9) to the assumption of Maxwellian distribution of energy amongst the vibrations of molecules. This assumption is probably not very far wrong in view of the fact that the specific heats of many organic compounds at room temperatures correspond to the participation of many of their vibrational degrees of freedom. That the decomposition rates of at least some molecules may be accounted for in this way is seen from the ostensibly suitable but experimentally difficult example of the straight chain paraffins (10).

Table 1

	Velocity constant	
	"Theoretical"	Observed
Propane	0.00235	0.0015
n-Butane	0.0047	0.0047
n-Pentane	0.0031	0.0036
n-Hexane	0.013	0.0094

The discrepancies between the "theoretical" and observed values are not substantially greater than the reproducibility of Frey's constants, although his experimental work is probably the most nearly quantitative in the field.

On the other hand, this point of view may represent an over-simplification and does not develop sufficiently the mechanism by which the vibrational energy is distributed (11).

The latter problem has been attacked repeatedly by various workers (12) because the new quantum mechanics has given a new tool for that purpose.

It seems that, on these theories, a given bond does not require a precise amount of energy before it can react but that there is some chance of it reacting with smaller amounts of energy provided there exists a state of the products with an energy content which is equal to a given state of the molecule. On this basis the term χ would involve the probability of such a transition and would moreover be related to the energy content of the molecule. Rosen has worked out numerical values for the life of the unstable molecule HO_2 in various initial states, the picture being that, when one of the bonds is in a state of high vibrational energy and the other in a low one, the latter can with high probability lose what energy it has and the first bond can simultaneously break to give fragments with the same total energy content.

The important point is that the new quantum mechanics appears to be capable of providing numerical values for such transition probabilities as well as for factors controlling the distribution of energy. It is also important that the new methods of calculation appear to do no particular violence to earlier concepts of the mechanism of chemical reactions which, however, admittedly were less articulate. That is, unless the reacting bond has concentrated within it almost the amount of energy which would have caused reaction on the old basis, it has a small chance of reacting according to the new quantum mechanics.

For bimolecular reactions between simple molecules χ appears to represent merely the number of collisions between reactant molecules. Although χ must include orientation factors in such cases, they turn out to be small. However, due to the short range of atomic forces, one would expect such factors to grow in importance for complex molecules, such as higher molecular weight olefines, which would be expected to polymerize at least in part by means of homogeneous bimolecular reactions.

There has been a tendency in the development of chemical kinetics to confine discussions and correlated experimental work to thermal decompositions and it has been concluded that for this type of reaction the simple molecules react bimolecularly and more complex ones unimolecularly. Presumably in the case of metathetical reactions more complex molecules, in so far as they react independently of catalysts, will do so in accordance with the bimolecular law. The proper investigation of this field has scarcely started (13).

The further review of the kinetic theory of reaction velocity would take us afield and would involve technical and sometimes controversial points. Suffice it to say that equation (I) adequately represents reaction velocities and is to a considerable degree understood and therefore points out the factors upon which catalysts may be expected to operate in influencing reaction velocities. It is appropriate to attempt to estimate the relation of the various factors represented in equation (I) as far as the scope for catalytic action is concerned.

While temperature and concentration are independent variables outside the sphere of catalytic action, a catalyst may change the functional relation of $\underline{f}$ ($\underline{c}$) between velocity and concentration and thus affect the reaction rate. This effect is ordinarily brought about, however, by the catalyst introducing a particular value of χ or E in equation (I) as applied to some component part of a complex reacting system which results in the effect, so that after all the effect of a catalyst appears to be limited to the terms χ and E.

At this point it is necessary to point out that so many new phenomena have been drawn into the field of catalysis that a definition of a catalyst which will cover all of them must be so broad that Hinshelwood suggests it is useless to make the attempt (14). Schwab (15), e.g., considers the action of hydrogen in keeping up the activation in certain unimolecular decompositions, when the reacting substance is at low concentration, to be an example of catalysis.

Our definition of a catalyst must cover at least the following:

(a) Positive and negative changes in reaction velocity.

(b) Change in course of a reaction as well as an alteration of the velocity of what was originally the dominant reaction. To cover all cases of interest (e.g., the polymerization of styrene) the end products need not be the same.

(c) The catalyst may or may not be used up in the reaction (e.g., inhibitors of certain auto-oxidation processes are themselves altered chemically).

(d) The catalyst may or may not play a stoichiometric part. (Thus in the H_2 - Cl_2 reaction, atoms of Cl or H are catalysts and form the ordinary compound HCl in the course of their action, although atoms are simultaneously generated in the act of forming the HCl.).

The factor χ includes any restraint which may be imposed by an orientation factor. The whole discussion may be simplified by discussing this factor separately. In the homogeneous cases so far studied orientation factors appear to be small (16).

Heterogeneous catalysts involve oriented adsorption and might be thought to diminish the restraint of orientation factors in the case of large molecules thereby. However not more than 1×10^{14} molecules can be accommodated on a square centimeter of surface, whereas a c.c. of gas at N. T. P. contains 2.7×10^{19} molecules. Also a molecule (of H_2) at N. T. P. experiences about 1.5×10^{10} collisions per second in the gas phase, and about one tenth of this number from the gas phase when it is adsorbed on a surface (according to kinetic theory formulae). In any case the latter number is smaller. These considerations would limit the possible opportunity for catalysts to affect reactions by this route to collisions wherein both molecules are adsorbed. However the mobility of such molecules may be highly restricted by the very forces which give rise to the adsorption, and this must be kept in mind in calculating chances of a catalyst operating by diminishing an orientation restraint.

It appears to the writer that a further simplification of viewpoint can be made by considering an activated molecule to be one which contains sufficient energy in the bond which is ruptured in the reaction. On classical theory this would be a definite physical state and the probability for reaction would be 0.5 and for reversion to some other state 0.5, i.e., they would also be definite. This procedure would then lump the other component parts of χ into those factors governing the rate at which active molecules may be formed. These include a further definite basic factor <u>Z</u>, the total number of collisions, and another definite factor

$$e^{-E/RT} (E/RT)^{0.5n-1} / (0.5n - 1)!$$

(where n is the total number of square terms possessed by the reactant molecules) giving the maximum fraction of the collisions Z which according to classical kinetic theory may supply energy E to one of the colliding molecules (assumed for simplicity to be of the same kind).

But the molecules obey quantum laws rather than classical laws and energy is not fully and freely distributed amongst degrees of freedom at collision nor amongst the internal degrees of freedom of a molecule between collisions. So two further mutually similar factors enter in. One, which we may call F_1, governs the probability of transfer of energy from molecule to molecule in a collision and the second, which we may call F_2, governs the probability for redistribution of internal energy in between collisions.

A summary of the state of knowledge of such restraint factors (by C. Zener) is included in this report.

The importance of such phenomena is well illustrated by the work of Rice and Byck (17), who were able to impinge molecular rays of acetone and dimethyl mercury upon a target of platinum which was held at 1600° C. without these compounds experiencing appreciable decomposition. From the heats of activation for the homogeneous decompositions of the substances (from separate experiments) Rice and Byck concluded that if the molecules striking the surface had attained temperature equilibrium with it, decomposition would have been observed. Since they did not take the time factor into account, whereas an extended resting time on the surface would increase the amount of decomposition and since they did not use the full number of internal degrees of freedom available in their calculations, it seems that Rice and Byck were extremely conservative in their conclusions.

Hinshelwood (18), from studies of the effect of iodine on certain homogeneous reactions and of several uncatalyzed homogeneous bimolecular reactions where the rate falls far short of the rate of collision between molecules which bring into the collision zone the requisite energy of activation, is inclined to think that the $\underline{F}_1$ factor may be much more important than has been realized and that the action of iodine as a homogeneous catalyst is in part to eliminate the restraint imposed by that factor, by increasing the perturbation between the two molecules, which according to quantum mechanics is necessary for the exchange of energy.

Redistribution of internal energy, in a complex molecule as portrayed in the paper of Rosen (12), would presumably be facilitated by a catalyst which would provide a proper perturbation between the component parts of such a molecule.

The relief of such restraints may constitute a general mechanism for both homogeneous and heterogeneous catalysts (19).

Ions would be suitable for supplying such perturbations and a review (by A. K. Brewer) of some evidence for their effect in catalysis is included in this report.

Quantum mechanics, as has been mentioned, provides for transitions which would be impossible on the classical basis. Thus an energy wall, which prevents a classical process which is not provided with adequate energy, will not completely prevent the process according to quantum mechanics. This "tunnel effect" is the basis of a theory of catalysis proposed by Born and

Weisskopf (20), according to which a catalyst may increase reaction rates by holding the reactants in proper juxtaposition for a time large compared with the duration of a collision. The chemical transition occurs by the process of quantum mechanical resonance, which may occur when there are corresponding energy levels in the reactant and transformed states. The part played by the surface may be to effect a proper adjustment in levels between the initial and final states or to supply the perturbation which is required for the resonance phenomenon.

Of course the rate at which the energy of activation is supplied may be increased if kinetic mechanisms are supplemented, e.g., by absorption of light, and the catalyst may be the agent by which this is accomplished.

This procedure is well illustrated by the photosensitizers of which mercury vapor is an example (21). Since research in this subject does not appear to be particularly active at the present time, it is largely neglected in this report.

By stretching the definition of a catalyst a little, the phenomenon of foreign gases keeping up the rate of unimolecular reactions at low concentrations of reactants may come under this division of catalytic action. It is stretching the definition of a catalyst (a) because the effort of the catalyst is no greater than, if as great as, that of the reactants themselves and (b) because the velocity will only be kept up to the "normal" value and not raised beyond it.

In this (   ) division of catalytic action it should be pointed out that there is a general factor operating which tends to balance the disadvantage of a catalyst due to the small fraction of reactant which is ordinarily adsorbed upon it at one time. This factor is the relatively large number of vibrations to which the adsorbed molecule is subjected. Thus, using the Lindemann method, Biltz (22) calculated the vibration frequencies for the elements and from his list we select platinum 4.36 x 10^{12} and carbon (graphite) 2.77 x 10^{13} vibrations per second. If it is then assumed that Maxwellian distribution of energy prevails amongst these vibrations it is evident that each adsorbed molecule will have many opportunities to receive energy from the surface as compared with the number of such opportunities in the gas phase (since as has already been pointed out a molecule even of the fast moving hydrogen experiences but 1.5 x 10^{10} collisions per second in the gas phase at N. T. P.) These considerations are of course complicated by the restraints previously mentioned which govern the transfer of energy.

In spite of the innovations in viewpoint introduced by the quantum mechanics and by the experimental evidence recently collected by Hinshelwood and his colleagues, the idea persists that the principal mode of action of catalysts consists in the lowering of energy activation (E). This is in essence a structural problem and involves on the one hand a proper visualization of the process of adsorption based upon the unwieldy mass of published work in this field, and on the other hand a rationalization of that picture with the developing ideas of nature of chemical bonds and the ways in which they can be affected.

With this background, the subject of catalysis may now be broken up into its component parts which will be treated in more detail and with the cooperation of various specialists more expertly.

Adsorption

Langmuir's (23) unimolecular film theory of adsorption should be considered as well established, since his own and various other measurements confirm it within the limits of its conception (24) and since even the predictions of the Polányi-Eucken potential theory (25) seem to correspond numerically to films about one molecule thick under the conditions under which the Langmuir theory is supposed to apply.

Langmuir's work on adsorption has met some criticism on the ground that in it he neglected the forces acting between adsorbed molecules. This point he has now incorporated simply by treating the heat of adsorption as a function of the surface covered rather than as a constant (26).

It so happens that, due to the studies of Langmuir on the one hand and Becker (27) on the other, the system cesium adsorbed on tungsten seems to be better understood than any other which has come to the writer's attention.

Becker concludes that both cesium atoms and positive cesium ions may exist on the surface. The positive ions act like a positively charged grid placed very close to the surface, and this gave him a means of estimating the relative numbers of ions and atoms on the surface. When the surface is completely covered with cesium, 23 per cent of this substance exists as ions. This fraction increases as the degree of covering decreases until when the surface is one-tenth covered, fifty per cent of the cesium exists there as ions. He further concludes that the work required to remove an adion from the surface increases while the work required to remove an adatom decreases as the surface concentration increases, and this has its natural effect upon the mean life of adsorbed particles. Surface migration of the adsorbed cesium was demonstrated. The relations were such that above a certain temperature every cesium atom striking the surface evaporated as an ion. This gave him an assured method of starting with a cesium-free surface.

Becker's experimental method of determining θ (the fraction of surface covered) consisted in observations of electron emission and time. He found, starting with a bare surface, that a maximum in electron emission occurred with time, and assumed that this maximum occurred when the surface was just covered with cesium. Above a certain temperature the equilibrium value of θ is less than one, and can be determined by lowering the temperature of the filament suddenly and measuring electron emission vs. time. The conclusion that maximum electron emission corresponded with complete covering appeared to be based on a correlation with the calculated number of cesium atoms which the surface could accommodate.

Langmuir and Taylor used two methods for estimating the amount of adsorbed cesium.

(a) The tungsten filament was flashed at a temperature above 1300°, whereupon every adsorbed atom evaporated as an ion and registered in the kick of a ballistic galvanometer.

(b) The second method consisted in evaporating the adsorbed cesium as atoms, in the presence of a retarding electric field which prevents the escape of ions. These atoms then fall upon a tungsten surface heated above 1300° from which they escape as ions and once again register in the kick of a ballistic galvanometer.

These methods involve two assumptions: (1) That the accommodation coefficient is unity; (2) That the number of cesium atoms striking the surface in unit time is given by the positive ion current drawn when the filament is sufficiently hot.

These authors (28) conclude that optimum electron emission occurred when the surface was 67 per cent covered with cesium instead of completely covered as assumed by Becker, and find certain general difficulties with his method.

Taylor and Langmuir conclude that their tungsten surfaces, prepared by heating to 2900° in vacuo, were etched with development of the dodecahedral crystal faces so that the true surface is 1.347 times the apparent surface. One half of one per cent of this surface is able to absorb cesium more firmly than the rest. When the monomolecular film of cesium is complete, there is one cesium atom on the surface for every four tungsten atoms.

It was found that the processes of condensation and evaporation proceeded entirely independently of each other, from which it was concluded that cesium atoms striking the surface ion slide around in a second layer until they find positions in a first layer. The number in the second layer at any one time was thought, however, to be minute. Like Becker, they conclude that the rate of evaporation of cesium atoms increases rapidly as the fraction of the surface covered increases, and they developed a quantitative theory for this effect.

They regard an adsorbed cesium atom on a tungsten surface as an ion held to the metal by its image force. This ion tends to draw induction electrons from the metal towards the ion.

The force between two such adion dipoles is given by

$$\underline{f} = 3/2\, \underline{m}^2/\underline{r}^2 ,$$

where $\underline{m}$ is the electron moment of the dipole and $\underline{r}$ the distance between them. An equation of state was then marked out to apply to the adsorbed cesium film by applying the Clausius virial equation, whereupon the equation

$$\underline{F} = \frac{\sigma k T}{(1-\theta)} + 3.34\ \sigma^{5/2}\, m^2 + 1.53 \times 10^{-5}\ \sigma^2\, \underline{T}^{1/3}\, \underline{m}^{4/3}\, \underline{I}$$

was obtained, where $\underline{F}$ is the spreading force, σ is the number of adsorbed atoms per sq. cm. of tungsten surface, θ is fraction of surface covered, and $\underline{I}$ is an integral whose numerical value can never exceed 0.89.

This spreading force is related to the rate of evaporation ν_a by means of the Gibbs equation

$$\frac{d\,F}{d \ln\ \nu_a} = \sigma\, \underline{k}\, \underline{T}$$

These relations serve as a means of calculating $\underline{m}$ from the evaporation rates.

A check of the values of $\underline{m}$ obtained in this way, against those obtained from measurements of electron emission, gave excellent agreement. The contact potential ν of a metal surface covered with an adsorbed film as compared with that of the bare metal surface is given by

$$\nu = 2\,\pi\,\sigma\,\underline{M}.$$

and the electron emission is related to the contact potential by means of the equation

$$\frac{\nu_e}{\nu_w} = \frac{\nu_e}{e^{KT}}$$

where $\nu_{\underline{W}}$ is the electron emission from pure tungsten, $\nu_{\underline{e}}$ is that from tungsten with adsorbed material upon it of dipole moment $\underline{M}$.

Assuming the correctness of these measurements and conclusions, it is evident that these workers have given us an extraordinary knowledge of the system cesium adsorbed on tungsten. While this system at the moment lends itself to no direct application in catalysis, nevertheless it is likely to serve as a base from which excursions into less tractable regions of surface action may be undertaken with more confidence. Thus we have here a surface of known area which is likewise known to act as a catalyst for certain reactions such as the thermal decomposition of ammonia.

The writer (29) in 1928 carried out experiments on the thermal decomposition of ammonia upon aged tungsten filaments. In this reaction the heat of activation must be supplied from the surface. Calculating the vibration frequency of the tungsten atoms from Lindemann's formula and neglecting all restraints upon energy transfer, and assuming this surface to be the same as that investigated by Langmuir, it turns out that the theoretical reaction rate is about seven times too fast if the reaction occurs exclusively on the major fraction of the surface and about 25 times too slow if it occurs exclusively on the minor fraction of the surface. The neglected factors necessarily influence the calculation in such a direction as to confirm the indication that the reaction occurs uniformly on the dodecahedral faces of the tungsten.

Measurement of Surface Area

In order to make a complete quantitative study of either adsorption or catalysis it is necessary to know the surface area and circumstances seldom permit as exact an estimate as that just considered. The methods available for this purpose may be summarized:

(1) From emission currents, as just discussed in the case of cesium or tungsten.

(2) The Paneth radioactive indicator method (30), which is strictly limited in scope.

(3) Bowden and Rideal's method (31), which depends upon the measurement of the change in electrode potential caused by the passage of a definite electric flux.

(4) Methods depending upon measuring the amount of some adsorbed substance upon surfaces of unknown area in comparison with that adsorbed upon a surface of known area (32).
This method involves uncertainties introduced by (a) the possibility of the adsorbed molecule occupying different areas on different surfaces, (b) the chance that some portions of the surface may be inaccessible to the molecule in question when it is large as in the case of Paneth's dye, (c) the chance that some elementary spaces even though accessible will not be covered by the molecule in question. This method (33), however, probably has the most general application.

(5) Schwab and Rudolph (34) have used a method of limited application, consisting of measuring the rates of solution of the finely divided adsorbent or catalyst, and assuming this to be proportional to the surface area. This evidently is based upon early knowledge (35) that such processes are limited in rate by diffusion, and therefore would lead to correct results only in case the diffusion blanket is uniform in thickness. This evidently cannot be true in the case of substances containing long fine pores, etc.

(6) Dunn (36) and Constable (37) have used a method of very limited

application which depends upon a knowledge of the thickness of Newtonian temper colors obtained upon metals, e.g., upon oxidation. From a knowledge of the total amount of oxygen absorbed the area of the surface can be estimated. This method is open to the objection that the oxide film probably is not uniformly thick.

Electrical Distortion Effects at Surfaces

The general idea that films are but one molecule thick is subject to the reservation that electrical distortion effects at surfaces may cause sufficient polarization to lead to multimolecular films, and we have seen that cesium adsorbed on tungsten is distorted to the extreme of ionization under certain circumstances. However, just as the effect in the cesium or tungsten did not lead to a second layer according to Langmuir (see however Becker), the gist of current work in this field appears to be that such phenomena do not in general lead to the formation of a second adsorbed layer under conditions where the second layer would not exist in the absence of these electrical effects (38).

Langmuir performed some calculations based on the work of DeBoer on the system iodine adsorbed on calcium fluoride. This is a case which is favorable for electrical deformation since iodine, being a large atom, is easily deformed (though not so easily, of course, as cesium). He concluded that the heat of adsorption in the nth layer is given by

$$b_n = b_s - 29 + 1800(0.5)^n ;$$

at 293° K the mean life of an iodine molecule in the first adsorbed layer came out to be 2000 seconds, so that the film would be stable at pressures as low as 10^{-3}Po, where Po is the vapor pressure of solid iodine. The mean life of isolated molecules in the second layer would be only 4×10^{-4} seconds and this layer would disappear at pressures less than 0.01Po.

Polanyi, too, on the basis of the theoretical work of Lennard-Jones and Dent is inclined to minimize the part played by electrical forces in surface phenomena (39).

Our whole attitude toward adsorption should be that the process in essence is a chemical reaction. The reactions do not appear to behave in the usual stoichiometric way, not because the forces involved are different in kind but because the number of surface atoms involved in the adsorption and also the ratio between the number of such atoms to the number of atoms of the solid catalyst vary from sample to sample. Also, due to the geometric arrangement of the surface atoms, distortions may be set up in adsorbed molecules which may give them properties which could not be predicted from the behavior of the molecules when not adsorbed. In view of the chemical nature of adsorption, it is not surprising to find that, like most chemical reactions, a heat of activation may be involved in the process of adsorption. The same molecular species could be adsorbed by a process involving activated adsorption under one set of conditions and at lower temperature, when the energy of activation may be but rarely supplied adsorption may be by means of Van der Waals' forces. Langmuir (40) seemed to have this in mind in 1918 but few people did, so that H. S. Taylor (41) was later able to show how the possibility of these two types of adsorption could explain various phenomena in adsorption and catalysis.

While Taylor's point of view has been supported by various experiments, there has also been opposition to it (42). Thus Allmand and Chaplin (43) suggest that the effects attributed to activated adsorption may be merely the slow displacement of some other film from the surface. This is no doubt a real phenomenon.

Ward (44) and also Steacie (44) suggest that the slow adsorption found in many of the above references and attributed to slow adsorption are due to diffusion into the adsorbent. Ward's experimental work is to be commended and he demonstrates this idea rather convincingly for the case of hydrogen adsorbed on copper. The diffusion is thought to be of the intergranular type and itself requires energy of activation.

In some of the work on slow adsorption which was attributed to required energy of activation (45), values of the energy obtained from the temperature coefficient of the process were of the order of 15,000 calories per gram molecules. Since a surface atom is struck about 1 x 10^9 times per second by H_2, at 0°C and one atm. pressure, reaction would be complete in a few minutes. This was appreciated by Taylor (46).

A similar point has been made (without, however, specifying the temperature to which his calculations referred) by Rideal (47).

The writer's point of view on "activated" adsorption is that there is no very good reason for doubting its existence. Both common sense and quantum mechanics allow for it. Whether or not the experiments advanced to illustrate it may be explained in other ways is a matter for careful consideration in each case. Theoretically one might also consider a surface (since it has free valences) as being similar to a free atom or a free radicle (48), and adsorption upon it might therefore require a minimum though not necessarily a zero heat of activation, as, e.g., when but one surface atom is engaged in the adsorption.

Taylor has summarized his own point of view and its quantum mechanical background, developed largely by his colleague Eyring, in the following section.

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ACTIVATED ADSORPTION

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Since the formulation of the concept of activated adsorption three years ago, a considerable body of experimental material (1) has been produced in support of the concept. The idea has also been subjected to a moderate degree of criticism and alternatives to the concept of activated adsorption, such as activated diffusion and solution, have been suggested. It may be advantageous to summarize the evidence adduced both in support of and antagonistic to the concept.

Experimental evidence of two types of binding of gases to surfaces is now available with respect to hydrogen, nitrogen, oxygen, carbon monoxide, water vapor, saturated and unsaturated hydrocarbons and nitrous oxide. The surfaces studied include metals such as nickel, iron, copper, palladium and tungsten, and oxides such as those of zinc, manganese, chromium, copper, molybdenum, aluminum and vanadium and mixtures of the same. The low temperature adsorption is usually spoken of as van der Waals' adsorption, has negligible activation energy and rapidly yields equilibrium values at carefully controlled temperatures. In the higher temperature ranges, the activated adsorption is characterized by a measurable rate of attainment of equilibrium, from which rates, at several temperatures, activation energies may be deduced. The following tables summarize the principal results of adsorption measurements with hydrogen, carbon monoxide and nitrogen at various pressures and temperatures. In the hydrogen table are given in the next to last column the available data on heats of van der Waals' adsorption (λ_v) and the heats of activated adsorption (λ_a).

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Table 1.

Hydrogen

Adsorbent	P mm.	Adsorption in cc. per 100 grams at T° C. =							λ x10^{-3} in Cals.	Ref.
		-185	-78	0	110	184	305	444		
Ni	100	16		70^a			54^b			2
	700	48		70^a			75^b			
Ni	25	8.6	27	23	15				$\lambda_a \sim 15$	3
	200	11	32.5	28	23					
	600	15	33	33	28					
Fe	600	160	0	0			100^c			2
	500	3.4	0.7	6						4
Cu	500	7.8	18.5	17.5					$\lambda_v = 1$ $\lambda_a \sim 10$	5
W	0.5			0.18	0.08	0.11	0.05		$\lambda_a \sim 8.6$	6
MnO	506		0	0		24	39	20		7
MnO - Cr_2O_3	165		23	15		345	364	217	$\lambda_v = 2$ $\lambda_a = 20$	7
ZnO	400	105	13.1	13	33	68	39		$\lambda_v = 1.1$ $\lambda_a = 21$	8
ZnO - Cr_2O_3	760	228	52	112	137	160	130			9
Cr_2O_3 gel	700	1350	91	22		200	200		$\lambda_v \sim 1.8$ $\lambda_a \sim 20$	10
ZnO - Mo_2O_3 ^{d}	100	8	0	0	0	5	13.5	16.0	$\lambda_v \sim 2$ $\lambda_a \sim 20$	11
V_2O_3	650			0		10	24.2	22.8		12
Al_2O_3	650			0	0	0	0	6.7		13

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a = 19°C., b = 336°C., c = 380°C., d = wt. unknown, e = 218°C.

Table 1 - Continued

Carbon Monoxide

Adsorbent	P mm.	Adsorption in cc. per 100 grams at T° C. = -185	-78	0	110	184	305	444° C.	Ref.
Fe	500	27.5	3.7 v >11.0 a	0.2 v >17.0 a					4
Cu	200	90	30	22	30				5
Pd	150	83	50	94	50				
MnO - Cr_2O_3	150	2250	530			670	320		15
ZnO - Mo_2O_3	600			2.8	0.5		1.5	0.9	11

Nitrogen

Adsorbent	P mm.	-185	-78	0	100	300	360	600	Ref.
Fe	700	24	4	<1			>1		4
W	1			0.03	0.07	0.53		1.00	6
		-189		+400	450°C.		$\lambda_a \times 10^{-3}$ in cals.		
Fe - Al_2O_3	700	393		44.8	36.1		λ_a = 35		15
Fe - K_2O- Al_2O_3	700	182		28.0	22.5		λ_a = 35		15
Fe (unpromoted)	700	17.2							15

Examination of the tables will show that activated adsorption, as revealed by a reversal of the change in quantity adsorbed with increase of temperature, may manifest itself throughout the temperature range of -110° to +450° C. It is also evident that the activated adsorption is quite specific and is not governed, as is van der Waals' adsorption, principally by extension of surface. The heats of activated adsorption of hydrogen are, in so far as they are ascertained, about one order higher than those of van der Waals' adsorption. It it this difference in the heats involved which is decisive in differentiating van der Waals' adsorption from the other process, whatever view may be adopted concerning the high temperature process, whether adsorption, diffusion or solution. Whatever it may be, it is not the ordinary classical adsorption.

Activation Energies of Activated Adsorption

In the first researches of Taylor and Williamson (16) it was shown that the promotion of manganous oxide by chromium oxide materially lowered the activation energy of the first hydrogen adsorbed. Also, it was shown that the activation energy increased with increasing extent of surface covered, a definite proof of nonuniform surface activity.

These points are more decisively demonstrated by some work by Taylor and Strother (17) dealing with activated adsorption of hydrogen on surfaces composed of zinc oxide, zinc and chromium oxides, and zinc and molybdenum oxides. In these experiments, performed at constant pressure, it has been shown that the velocity of hydrogen adsorption is a function of the surface, that the activation energy is determined in magnitude by the nature of the surface and that the activation energy required increases with increasing surface covered. With zinc oxide the activation energies range from 7 to 15 kg.-cals. between the adsorption limits of 8 to 24 cc. per 100 grams ZnO. With zinc-chromium oxide the activation energies range from 1 to 12 kg.-cals. with activated adsorptions of 40 to 120 cc. per 100 grams $ZnO-Cr_2O_3$. With the zinc-molybdenum oxide sample the activation energies range between 17 and 33 kg.-cals. between the adsorption limits of 0.4 to 8.5 cc. per 100 grams $ZnO-Mo_2O_5$. Some unpublished work of ours indicates that the activated adsorption of carbon monoxide parallels that observed with hydrogen on the three surfaces but that the activated adsorption of carbon monoxide is the slower process. The close parallelism between these results and the facts of methanol synthesis are also apparent. It is well known that this synthesis is enormously more rapid on zinc-chromium oxide surfaces than on zinc oxide surfaces. It is not so well known, but equally true, that surfaces of zinc and molybdenum oxides are much inferior to zinc oxide in the same synthesis. It may be that the rate of methanol synthesis may be controlled by the velocity of activated adsorption of the reacting gases. In the synthesis of ammonia there is definite evidence that the rate-determining step is the activated adsorption of nitrogen. This was pointed out by Taylor in the original discussion of activated adsorption and has now been experimentally confirmed by Emmett and Brunauer (18).

It was pointed out by Taylor (19) that the measured velocity of activated adsorption of hydrogen by zinc oxide was far smaller than would be expected on the assumption that adsorption occurs when gas molecules, with an energy equal to the observed activation energy, strike the surface. This observation also holds for the nitrogen adsorption just cited and also for the hydrogen adsorptions at constant pressure on the three surfaces studied by Taylor and Strother (17). These latter data permit a more penetrating analysis of the problems. If we assume that the velocity of adsorption $\underline{v}_1$ on a surface of which the activation energy is $\underline{E}_1$ is given by the expression

$$\underline{v}_1 = \underline{Z}\,\phi_1 \underline{e}^{-\underline{E}_1/\underline{RT}}$$

where $\underline{Z}$ is the kinetic collision factor per unit area of surface per unit of time; the quantity ϕ_1 must contain the surface area on which the magnitude of the activation energy is $\underline{E}_1$. On another surface area with activation energy $\underline{E}_2$ the velocity of adsorption will be

$$\underline{v}_2 = \underline{Z}\,\phi_2 \underline{e}^{-\underline{E}_2/\underline{RT}}$$

The experimental data of Taylor and Strother at constant pressure, and therefore constant $\underline{Z}$, permit a determination of the ratio ϕ_1 to ϕ_2 from actual measurements of $\underline{v}_1$, $\underline{v}_2$, $\underline{E}_1$ and $\underline{E}_2$. Calculations of this ratio show that, on a given catalyst surface, as $\underline{E}$ increases, the ratio $\phi_1 : \phi_2$ also increases and at an exponential rate. Thus, with both zinc oxide, and zinc oxide - molybdenum oxide surfaces a plot of log ϕ_1/ϕ_2 against $\underline{E}$ gives a good straight line. With zinc chromium oxide surfaces ϕ_1/ϕ_2 decreases as $\underline{E}$ increases from 1 to 5 kg.-cals. but at still higher activation energies the same exponential increase of $\phi_1 : \phi_2$ occurs. These results indicate that on zinc oxide and zinc oxide - molybdenum oxide the areas with the smallest activation energies are the least numerous. On the zinc-chromium oxide studied, surface areas with an intermediate activation are the least numerous. The actual data are collected in Table 2. The values of $\phi_1 : \phi_2$

do not measure the relative areas with given activation energies since the quantity, ϕ, must include not only the surface area in question but also the fraction of the area which is occupied by gas. At the moment there does not seem to be any way of separating these factors.

Table 2

Zinc Oxide		Zinc-Chromium Oxide		Zinc-Molybdenum Oxide	
E in Kilo Cals.	Log ϕ_1/ϕ_2	E in Kilo Cals.	Log ϕ_1/ϕ_2	E in Kilo Cals.	Log ϕ_1/ϕ_2
7.7	0	1.4	1.57	17.2	0
9.0	0.4	2.2	0.83	18.6	0.5
10.0	0.5	4.2	0.15	23.4	2.7
11.0	0.9	5.8	0	27.3	4.4
13.5	2.0	8.0	1.36	28.5	4.5
17.3	3.5	10.8	2.91		
		11.0	3.02		
		12.0	3.15		
		13.0	3.3		

This exponential relationship between ϕ and E in activated adsorption is also found in the kinetics of heterogeneous reactions as has been emphasized by Schwab and Cremer (20) for decomposition reactions on various sintered oxide and halide surfaces, by Balandin (21) on unsintered metallic catalysts for dehydrogenation reactions and quite recently by Eckell (22) on surfaces of iron oxide - alumina in the reaction of carbon monoxide and oxygen. Howard (23) has compared the velocities of adsorption of hydrogen on different oxide surfaces and has also shown that the effect of a high value of E is always compensated for by a correspondingly large value of what we have here defined as ϕ. Benton (24), however, in a recent study of the activated adsorption of oxygen on silver concludes that the activation energy is constant over the range of adsorptions studied and observes that a proportionality factor, A, (the $Z \phi$ of the preceding discussion) connecting v and the exponential $e^{-E/RT}$ steadily decreases, and by large amounts, as the surface becomes increasingly covered. Benton calculates that, initially, every collision with energy in excess of the determined activation energy results in activated adsorption. He cannot account, however, for a decrease in the value of A from 10^9 to 10^5 when only half the surface has been covered. He believes, however, that the 50 per cent increase in the activation energy which would be necessary to account for this result certainly does not occur. It should be observed that, if the data of Taylor and Strother on oxide surfaces were treated in the same manner as that used by Benton, and it was assumed that the activation energy did not increase with increased covering of the surface, the experimental data would yield precisely the same result as obtained by Benton. The value of A, the proportionality factor, would decrease by many orders before appreciable fractions of the surface were covered. It may therefore be that the correct interpretation of the velocity of activated adsorption lies between the two extremes here discussed, namely Benton's view of constant E and rapidly falling A and the results which come directly from the experimental work of Taylor and Strother, which point to a steadily increasing value of E and a simultaneously increasing value of A. Experiments of still greater accuracy than those hitherto conducted will be required to decide between such alternatives.

Quantum Mechanical Interpretation of Activated Adsorption.

The newer developments in quantum mechanics applied to chemical reactions permit a theoretical approach to this problem of activation energy of adsorption and the effect of surface configuration on its magnitude. The energy of interaction, $W(r)$, between two atoms at a distance, r, consists of two parts, that due to the ordinary classical coulomb forces $A(r)$ and a nonclassical interchange energy $\alpha\ (r)$ which is positive or attractive in a stable diatomic molecule but may also be negative and repulsive at all distances r.

$$W(r) = A(r) \pm \alpha(r)$$

London (25) extended these ideas to systems of three atoms and was followed by Eyring and Polányi (28) who derived an expression for the energy of a system of three atoms X, Y and Z in terms of the coulombic energies A, B and C of the three pairs of atoms XY, YZ, and ZX and the interchange energies α, β and γ of the same pairs; $A + \alpha$, $B + \beta$ and $C + \gamma$ being the bond energies of the respective atom pairs when the third atom is at infinite distance. For such a system the energy W_3 is

$$W_3 = A + B + C + \left\{1/2\left[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2\right]\right\}^{1/2}$$

The bond energies of atom pairs at various distances are obtainable either from spectroscopic data or, as was suggested by Eyring, from potential energy curves of diatomic molecules with the aid of the empirical equation, due to Morse (26) which expresses the potential energy by means of the equation

$$W = D'\ (e^{-2a(r - r_0)} - 2e^{-a(r - r_0)})$$

Here D' is the heat of dissociation of the molecule plus the zero point energy ($= 1/2\ h\gamma$), r is the nuclear distance, r_0 the equilibrium nuclear distance of the molecule, a is a constant and equal to $0.1227\ \omega_0\ (M/D')^{1/2}$ where M is the reduced mass and ω_0 is the classical frequency of vibration. In this equation, ω_0 is expressed in wave numbers per cm., and r and r_0 in Angstrom units, the potential energy of the two atoms at infinite distance being chosen as zero. The energy values derived from such a curve at various distances give the sum of the coulombic and interchange energies, for example, $A + \alpha$. To apply the energies so obtained to the expression for the energy of three atom systems it is necessary to know the fractions of the total energy which are respectively coulombic and interchange. From Suguira's calculations for the hydrogen molecule, the coulombic part in this case is approximately ten per cent of the total.

Eyring and Polányi (28) were therefore in a position to apply the equation to the three atom problem

$$H_{2\,\text{para}} + H = H_{2\,\text{ortho}} + H$$

making use of the data from the Morse curve on the basis of 10 per cent coulombic energy. An examination of the equation in an alternative form

$$W_3 = A + B + C \pm (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \alpha\gamma - \beta\gamma)^{1/2}$$

shows that less energy will be required for the approach of a third atom to a molecule if the three atoms are in a straight line configuration. Eyring and Polányi, therefore, computed the energies of various linear systems of three hydrogen atoms for various interatomic distances r_1 and r_2. The solutions of the equation when plotted in a two-dimensional diagram having $\underline{r}_1$ and $\underline{r}_2$ as ordinates and abscissae could be recorded in the form of contour lines of equal energies, representative of a potential energy surface. This surface resembles two long deep valleys separated by a mountain pass, the height of which, about 13 kg.-cals., represents the calculated activation energy of the process, to be compared with the experimental value of 7.25 kg.-cals. Pelzer and Wigner (29) have made a more extended application of the equation to this reaction and were able to deduce not only the activation energy but also the actual rate of reaction.

Eyring (30) applied this equation also to other three univalent atom systems and then employed the same treatment for four atom systems, the potential energy equation for which is

$$\underline{W}_4 = \underline{A}_1 + \underline{A}_2 + \underline{B}_1 + \underline{B}_2 + \underline{C}_1 + \underline{C}_2 + \Big\{1/2 \Big[(\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2\Big]\Big\}^{1/2}$$

in which $\underline{A}_1$, $\underline{A}_2$, $\underline{B}_2$, ----- and α_1, α_2, β_1, etc. refer to coulombic and exchange energies between the six atom pairs. The extension of this method of attack to adsorptions at surfaces was initiated by Sherman and Eyring (31). They considered the four atom system composed of a hydrogen molecule approaching two fixed carbon atoms in a surface of charcoal. The adsorption process is assumed to replace a single H - H bond of 103 kg.-cals. and a weaker bond between carbon and carbon by two C - H bonds whose combined strength exceeds the energy of the bonds broken by an amount equal to the heat of adsorption.

Sherman and Eyring calculated the energy $\underline{W}_4$ for various carbon-carbon distances and for various positions of the approaching molecule. Thence it was possible to deduce the easiest energy path from the state of molecular hydrogen to that in which each hydrogen was attached to one of the carbon atoms. They found that the activation energy required was very sensitive to the carbon-carbon distance in the solid body. With too small an atomic distance in the solid the activation energy is high because of the operation of repulsive forces among the four atoms. With large atomic distances in the solid the activation energy will also be high since the process practically involves the complete separation of the atoms of the hydrogen molecule. At some intermediate distance the activation energy will pass through a minimum. It is this distance of minimum activation energy which determines the most active centers. Other surface atom distances, whether greater or smaller, require higher activation energies. The surface atoms with the most favorable distance are those which will first be occupied during activated adsorption. The greater the deviation of two surface atoms from this most favorable distance, the higher the activation energy. Conversely, a completely uniform space lattice would be necessary for an activation energy of adsorption constant over the whole range of adsorption. The concept of active centers on a catalyst surface is, on this theory, to be interpreted as involving those surface positions where the activation energy of adsorption or desorption is a minimum. The most favorable spacing will, of course, be some function of the chemical nature of the surface atoms.

The four-atom treatment of the problem of activated adsorption is an over-simplification of the actual problem, necessitated at the outset by the difficulties of theoretical treatment. The experience recently obtained in treating 6, 7 and 8 atom systems promises, however, to permit the theoretical study of the approach of a hydrogen molecule to an actual lattice surface. There is, however, no priori reason for believing that the lattice distance will be any the less important in the many-atom system.

Variations from the normal lattice distance in incompletely crystallized units or surfaces, such as may very probably result from the usual methods of preparation of active catalysts, is indicated by the calculations of Taylor, Eyring and Sherman (32) on the binding energies of crystal nuclei. It was there shown that the lattice distances for the most stable arrangements of 4, 5, 6, 7 and 8 atoms might differ markedly from the normal lattice distance of the bulk crystal. Such variations in atomic distances will be associated, as has been shown, with variations in the activation energy. The recent evidence of Eckell (33) on the improvement in the catalytic activity of nickel foil in the hydrogenation of ethylene, due to cold working, is attributed by him to the changes from the normal atomic distances of the catalyst atoms brought about by the treatment to which the foil is subjected. Eckell shows that this increased catalytic activity is eliminated by annealing the nickel at temperatures between 200 and 300° C. It is known that these temperatures are far below the recrystallization temperatures of the metal (600 - 700° C.), so that it would appear that the heat treatment which destroys the catalytic activity actually involves a release of the atoms from their abnormal and active distances to normal and less active distances. This effect of temperature on active catalysts is very familiar and has hitherto been known as sintering (34). It occurs markedly with active reduced copper and nickel around 200° C. and is accompanied by marked reduction in catalytic activity. This sintering may be regarded as a readjustment of the abnormal atom distances of high activity to the more normal lattice distances of lower activity.

Alternatives to Activated Adsorption

Ward (35) and Steacie (36) have assumed that the results on the slow sorption of gases by various metals and oxides can all be explained by activated diffusion along Smekal cracks or by true solution processes. It has also been maintained by Burrage (37) that slow sorption at high temperatures may be due to the presence of impurities which can only be displaced from the surface with difficulty.

The results of a recent research by Howard (38) dispose of all these alternative hypotheses, at any rate for the particular surface of chromium oxide used by him. Howard shows that the van der Waals' and the high temperature adsorptions are not additive. The latter profoundly modify the former, and the rapid van der Waals' adsorption is unaffected as to speed of attainment of equilibrium by previous activated adsorption of hydrogen. The low temperature equilibrium data are also entirely unaffected by a sequence of "flushing out". Howard also shows how his data on van der Waals' and slow adsorption are irreconcilable with the concept of activated diffusion into less accessible portions of pores or cracks. His results can only be interpreted on the assumption that activated adsorption is a true surface process and that its slow rate is not due to penetration into deeper parts of the mass than are accessible to rapid van der Waals' adsorption.

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DIFFERENTIAL HEATS OF ADSORPTION

One of the phenomena which H. S. Taylor sought to explain by means of "activated" adsorption was the "differential heat of adsorption" curves obtained in his laboratory and elsewhere (1), which curves often contained a maximum which it was thought might have a profound correlation with surface catalytic activity.

However, so many of the reported phenomena have been found in one laboratory and denied in another (2), so many sources of experimental error have been pointed out (3) and so many ways of explaining the results in case they are real have been suggested (4) that the subject is about as confusing and controversial as economics. With inhomogeneous surfaces, the casual expectation would be for the first material adsorbed to evolve the greatest amount of heat. However, other factors come in. In this case they are:

(1) Endothermic activation of the adsorbed molecules.

(2) Kinetic complexity of the adsorption process.

(3) Part played by intermolecular forces of the adsorbed molecules.

(4) Polarization of the adsorbed molecules.

(5) Energy of activation for the adsorption process.

Inhomogeneity of Surfaces

There have been various interesting investigations in adsorption in which it has been found that, by preparing surfaces properly and by taking a sufficient number of points, the adsorption isotherms obtained are not the smooth curves to which we have been accustomed but contain many sharp breaks, which may become as rectangular as those found, e.g., in dehydration of substances possessing more than one hydrate and often offered as proof of a "true" chemical compound as distinct from an "adsorption" compound (5).

While some of these authors (6) advanced special explanations for the "breaks" obtained in the adsorption, the explanations in so far as they are valid appear to come under the broad terms of Langmuir's elementary space theory of surfaces and the writer prefers to regard them in this light. The rectilinear nature of the adsorption isotherms obtained especially by Burrage is, however, very striking.

Any work such as this which increases our knowledge of surfaces or may be capable of so doing is of course of great interest to the subject of catalysis wherein we know that the surfaces are not necessarily uniformly active, and that therefore one state of the same matter is a better catalyst than some other state. Conclusions relative to the optimum state will be reserved until the mechanism of activation by catalysts can be discussed.

To decide what a probable mechanism for activation by catalysts should be, it is desirable to understand what we can of the nature of chemical bonds. It is not too much to say that our understanding was completely inadequate before the advent of the new quantum mechanics. The position of the matter at the present time will now be presented. In the United States, R. S. Mulliken on the one hand and L. Pauling on the other, have been active in the field. Mulliken and G. W. Wheland have cooperated in the organization of this report by summarizing these respective developments.

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THE NATURE OF CHEMICAL BINDING

PART I

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The electron structures of atoms and the periodic systems of the elements are now rather well understood as a result of the development of the quantum theory. According to its older form, the Bohr theory, each electron is assigned to an orbit. The number of electrons which can occupy the same orbit is, however, limited, and when this limit is reached, a "closed shell" is said to exist. Further electrons must go into the next shells. Similarities of outer-electron orbits in heavier atoms to inner-shell orbits which in lighter atoms are occupied by outer electrons, account for the periodicities of physical and chemical properties observed in the periodic system.

In the newer form of the quantum theory, the quantum mechanics, we no longer assign each electron to a sharply-defined orbit, but instead to a function of the electron's space coördinates which may be called an orbital: each orbital is a characteristic function of a suitable Schrödinger equation. We can use these in thinking much as we use orbits in the Bohr theory. The square of the numerical value, at any given place, of the orbital which an electron is occupying, gives the probability of finding the electron there.

It should be noted that, although at any instant each electron may be assigned to a definite orbital, frequent exchanges of electrons take place, so that in time each electron runs through the whole gamut of orbitals which are occupied in the particular atom in question. It should be further noted that, even when a definite set of orbitals (an electron configuration) has been specified, through which the electrons may roam, there are in general several modes of interaction between electrons occupying different orbitals, resulting in the existence of several possible states of the atom-as-a-whole. These differ in energy by fairly considerable amounts; for example, in the case of the nitrogen atom the electron configuration $(1s)^2(2s)^2\ (2p)^3$ gives three states, namely a ^4S with energy zero (normal state), a ^2D with energy 54.6 kcal. per mol and a ^2P with 82.0 kcal. The use of the above conceptions of atomic orbitals, electron configurations and states gives us fairly good but still only approximate descriptions of the electron structures of atoms.

For describing the electron structures of molecules, several methods are worth considering. Some of them regard molecules merely as modified collections of atoms or ions, and give descriptions using atomic orbitals. Others describe molecules in terms of molecular orbitals; these are used in the same general way as that in which atomic orbitals are used for atoms.

Before discussing molecules in general, we may well seek to distinguish between those with ionic and those with covalent binding. We realize, of course, that both types of binding may occur in the same molecule; also, more especially, that ionic and covalent binding are only two ideal limiting cases, most actual molecules belonging to intermediate cases.

In the pure ionic type, - an ideal never quite realized in practise, - we assign part of the electrons to orbitals of one or more positive ions, the rest to orbitals of negative ions. The chemical energy here is the electrostatic energy of attraction of oppositely charged ions, minus the net energy required to produce the ions from neutral atoms. The effect of the electrostatic attraction in ionic binding is limited by the fact that, at close range, repulsions spring up which finally balance the attractive forces. These repulsions are of the same general nature as the forces which act in covalent binding.

Turning now to covalent binding, there are several methods of describing it approximately by using orbitals. One of these is obtained by regarding a molecule as built up from two or more atoms, each with a definite electron configuration and in a definite state. This is the basis of the valence theory of London and Heitler, which, although it makes prediction which agrees rather well with chemical rules of valence, is, in general and on the whole, not nearly so good as certain others.

Another theory, which like the preceding is a generalization of the Heitler-London theory of the hydrogen molecule (the two become identical for that relatively simple case) is that developed by Pauling and by Slater. This also describes molecular electron structures by assigning the electrons to a definite electron configuration for each of the several atoms, but without supposing these atoms to be in any of their ordinary states; instead a certain artificial average state of each atom is assumed, which Van Vleck calls the valence state.

Of the various electrons assigned to each atom, of course, only one or a few function as valence electrons. In the theory, each valence electron pairs off with a valence electron of one of the other atoms. Thus we have quantum-mechanical electron-pair bonds which correspond well to the electron-pair bonds of G. N. Lewis in the case that the two electrons of the Lewis pair are equally or nearly equally shared between the atoms which they bind (examples H:H, Cl:Cl, $\mathrm{Cl{:}\overset{Cl}{N}{:}Cl}$). If the electrons in the Lewis bond are unequally shared, as in HCl, ICl, NH_3, the Slater-Pauling electron-pair requires an ionic correction (see below) in order to correspond well to the Lewis pair.

In the Pauling-Slater theory, one electron of a bonding pair is initially assigned to a definite orbital of one atom, the other to an orbital of another atom. The bond may be said to result from a quantum-mechanical resonance between the two electrons, characterized by their frequent interchange between the two orbitals. This is accompanied by a change in energy. The interchange frequency and the energy effect become large if the atoms approach closely. The resonance interaction can occur in either of two ways (a) the two electrons move in such a way that they spend most of their time fairly near together in the region between the two atoms; (b) they tend to stay far apart, and spend most of their time on the back sides of the two atoms. In (a), the average force produced by the electron-pair causes the two atoms to be attracted toward each other, giving a stable electron-pair bond. The nature of this might perhaps be suggested by writing it, for a molecule A_2, in the form of $A\ |X|\ A$. In (b), the net result is that the two atoms repel each other. This type of quantum-mechanical description and interpretation was first given by Heitler and London in their theory of the formation of H_2.

We turn now to another method, or group of methods, for approximately describing the electronic structures of molecules, developed principally by Hund and Mulliken. The method was first used for diatomic molecules, and was very successful in connection with the interpretation of their spectra, and in explaining some of their other properties (e.g., molecular ionization potentials, paramagnetism of O_2). The essence of the method is the treatment of molecules as independent entities, instead of as groups of atoms. The electrons were assigned to <u>molecular</u> orbitals. A molecular orbital is, in general, a function extending over a whole molecule, or at least over more than one atom, whereas an atomic orbital is localized in the neighborhood of a single atom. The method began, somewhat earlier than Heitler and London's treatment of H_2 using H atom orbitals, with Hund's discussion of H_2^+ and H . Later it was extended by Mulliken and Hund to heavier diatomic molecules, and there showed various regularities closely related to chemical ideas of valence. These relations were clearly formulated by Herzberg.

An important modification of the method was introduced by Lennard-Jones, who pointed out that it is much better to assign only the valence electrons in molecules to molecular orbitals, but to assign the nonvalence electrons to atomic orbitals. [More accurately, it is the <u>shared</u> electrons, rather than the "valence" electrons, which should be assigned to molecular orbitals; the shared electrons include the valence electrons, but sometimes also certain others which are especially strongly influenced by neighboring atoms.] In the present-day "method of molecular orbitals", Lennard-Jones' modification has been adopted. This method, which might more accurately be called the method of "atomic and molecular orbitals", thus differs from the method of atomic orbitals, — which includes among other things the case of ionic molecules and the Pauling-Slater treatment of electron-pair bonds, — only in respect to the manner of describing shared electrons. The two methods, as we shall see, give different approximations to the true electronic structures of molecules. Neither gives perfect approximations, but each has certain advantages, including that of relative simplicity. Actually the true structures lie between those given by the various approximations, but unfortunately cannot be simply described.

The method of molecular orbitals can best be explained by considering diatomic molecules first. Here we may distinguish <u>bonding</u> and <u>anti</u>-bonding molecular orbitals; one may also speak of non-bonding orbitals, but these prove to be atomic. In this theory, the Lewis electron-pair bond finds its quantum-mechanical analogue in a pair of equivalent electrons occupying a bonding molecular orbital. For a molecule A_2, the nature of this pair might be suggested as follows: A  A. Every bonding molecular orbital is of such form that it gives the electron a considerable probability of being found in any of various regions surrounding both nuclei, but with a pronounced emphasis on those parts of space which are between the nuclei. For brevity we may call an electron which occupies a bonding orbital a bonding electron. Every bonding electron gives rise to a net force of attraction between atoms.

In the method of molecular orbitals, the primary unit of chemical binding is a single bonding electron. When this is present alone, as in H_2^+, we have a "one-electron bond". Nearly always, however, we find bonding electrons in pairs. Thus we have the electron-pair bond as a secondary unit. Its much greater prevalence, as compared with the primary unit, among ordinary chemically stable molecules, may be attributed to the fact that it takes two bonding electrons to form a closed shell (or in some cases more), so that when atoms combine, the most stable arrangements are nearly always those in which advantage is taken of the opportunity of putting two electrons into each bonding orbital which is occupied at all.

Anti-bonding orbitals are of such forms that an electron occupying one has a greater probability of being found behind one of the two nuclei than between them. Thus the presence of anti-bonding electrons tends to produce a repulsion between the atoms which they connect. Anti-bonding electrons often occur in stable molecules, but only in company with a greater number of bonding electrons.

The following examples will make the preceding discussion clearer. Molecular orbitals are denoted by underscoring; of these the anti-bonding ones are indicated by an asterisk, the rest being bonding; atomic orbitals are given in ordinary type. The electron configuration is given first, then the electron state of the molecule-as-a-whole.

H_2^+, $\underline{\sigma\ 1s}$, ${}^2\Sigma_g^+$

H_2, $(\underline{\sigma\ 1s})^2$, ${}^1\Sigma_g$

He_2^+, $(\underline{\sigma\ 1s})^2\ (\underline{\sigma\ {*}1s})$, ${}^2\Sigma_u^+$

Li_2, $(1s)^2(1s)^2\ (\underline{\sigma\ 2s})^2$, ${}^1\Sigma_g^+$

N_2, $(1s)^2(1s)^2(2s)^2(2s)^2\ (\underline{\pi\ 2p})^4(\underline{\sigma\ 2p})^2$, ${}^1\Sigma_g^+$

O_2^+, ... $(\underline{\sigma\ 2p})^2(\underline{\pi\ 2p})^4(\underline{\pi{*}2p})$, ${}^2\Pi_g$

O_2, ... $(\underline{\sigma\ 2p})^2(\underline{\pi\ 2p})^4(\underline{\pi\ {*}2p})^2$, ${}^3\Sigma_g^-$

F_2, ... $(\underline{\sigma\ 2p})^2(2p\ \pi)^4(2p\ \pi)^4$, ${}^1\Sigma_g^+$

H_2^+ has a one-electron bond (one electron occupying the molecular orbital called σ-1s); H_2 has an electron-pair bond (two such electrons). The stable ion He_2^+ has an electron-pair bond like H_2, partially offset by an anti-bonding electron σ-*1s, giving a net effect similar to that of the one-electron bond in H_2^+. Li_2 has an electron-pair bond similar to that of H_2, but much weaker.

N_2, as formulated above, has six bonding electrons, although the real structure could be somewhat better described by a somewhat different formulation in which the electrons assigned above to 2s atomic orbitals are assigned instead to molecular orbitals. The six bonding electrons in N_2 as formulated above correspond to the chemical triple bond. It will be noted that these three pairs of electrons are not all equivalent. One pair occupies a σ type of orbital, while the other four electrons occupy a π orbital.

For single electron-pair bonds (cf. H_2, Li_2, F_2) the σ type gives stronger bonding than would the π type of orbital, so that single bonds in ordinary molecules are always of the σ type. Since, however, it can be shown that only one σ electron-pair is possible between two given atoms, any further bonding, as in double or triple bonds, has to be done by π bonding orbitals. Each of these can hold up to four electrons; four make a closed shell, and correspond to two Lewis electron-pair bonds. For atoms not close together, π bonds are much weaker than σ bonds, but when atoms approach very closely, as in N_2, π bonds become almost as strong as, or possibly sometimes even stronger than, σ bonds.

In O_2^+ and O_2, respectively, one and two electrons in an anti-bonding π orbitals are added to the N_2electron structure. Thus in O_2 we have a group of six π electrons assigned to molecular orbitals, four being bonding and two anti-bonding. The net effect is much the same as if there were a single bonding π electron-pair. This and the σ bonding pair together constitute the O_2 double bond. The paramagnetism of O_2 is a result of the fact that the two anti-bonding π electrons $(\pi^*2p)^2$ do not constitute a closed shell, and thus are free to arrange themselves in such a way that a triplet state is the normal state of O_2.

In F_2 the eight π electrons are nearly non-bonding and are best assigned to atomic orbitals, leaving the pair $(\sigma 2p)^2$ to form the single bond. Each of the other homopolar halogen molecules Cl_2, Br_2, I_2 has a $(\sigma\, \underline{n}p)^2$ bond like F_2 ($\underline{n}$ = 3,4,5 for Cl,Br,I). Similar analogies hold in other columns of the periodic system.

In all homopolar molecules, the bonding molecular orbitals have a form which is symmetrical relative to a median plane perpendicular to a line joining the two nuclei which are held by the bond. In heteropolar molecules (*e.g.* CO,NO,ICl) the bonds are of the same general type as in isoelectronic or in chemically homologous homopolar molecules, and can be described by the same kind of assignments of electrons to molecular orbitals, *e.g.* $\pi^4\sigma^2$ for CO, $\sigma^2\pi^4\pi^*$ for NO, σ^2 for ICl (cf. N_2, O_2, F_2). The only important change is that the molecular orbitals of unsymmetrical molecules are unsymmetrical, being relatively weaker near the electropositive, relatively stronger near the electronegative atom. One might suggest this, for a molecule with a single bond, by a symbol such as I ═⊃Cl. The degree of displacement of the center of gravity of the molecular orbital toward the more electronegative atom, and the electric moment of the orbital and of the bond, are probably all proportional to the difference in electronegativity of the two atoms.

The method of molecular orbitals is capable of describing by a single scheme the whole range of types from pure homopolar (*e.g.* I_2) through moderately polar (*e.g.* ICl) to the most nearly pure ionic (*e.g.* CsF). The bonding orbital gradually shifts its center of gravity, finally passing in the pure ionic limiting case into an atomic orbital of the negative ion, the shared electron-pair thus becoming a pair of electrons attached to the negative ion. This transfer, however, it may be noted, is still by no means complete even in (the diatomic vapor of) the most extreme ionic type existing (CsF).

The preceding description of the electron-pair bond in molecules of varying polarity is evidently a satisfactory quantum-mechanical equivalent of Lewis's earlier and more schematic description of the gradual shifting of a bonding electron-pair from a location of equal sharing in non-polar molecules (A:A or A:B) to one of unequal sharing in somewhat polar molecules (A:B) and finally to a state of allegiance to the electronegative atom in A^+B^-. The Pauling-Slater method, on the other hand, is directly applicable only to purely non-polar bonds. It can be applied to partially polar bonds only by adding an ionic correction term; *i.e.* $A = \!\!\!\subset B$ of the molecular orbital method or A:B of Lewis corresponds to $\alpha(A \boxtimes B) + \beta(A^+B^-)$, with $\alpha > \beta$ if the bond is near the non-polar case, $\beta > \alpha$ if it is near the ionic extreme. The quantum-mechanical linear combination of $A \boxtimes B$ and A^+B^- implies that the two electrons behave for a fraction of the time as if they were in a covalent bond $A \boxtimes B$, the rest of the time as if belonging to the ion B^-. The resulting total behavior is nearly the same as that given by the formulation using molecular orbitals.

The preceding discussion of the method of molecular orbitals has so far been in terms of diatomic molecules. Its generalization to cover polyatomic orbitals has taken two forms: (1) the use of localized (i.e. diatomic-type) molecular orbitals for shared electrons, each such orbital connecting just two atoms and having a form similar to that of a diatomic orbital; and (2) the use of non-localized molecular orbitals, each connecting two or more atoms. The first method was developed mainly by Hund, the second mainly by Mulliken.

The results obtained by the method of localized molecular orbitals are, to a large extent, similar to those already described for diatomic molecules: single bonds are always formed by a pair of electrons occupying a σ orbital, while double or triple bonds involve in addition two or four electrons occupying π orbitals. The designations σ and π are here used in a slightly approximate sense, first introduced by Dunkel with the symbols $[\sigma]$ and $[\pi]$, but they represent types very similar to the diatomic types properly called σ and π. With polyatomic molecules new results in regard to directional and similar properties of bonds also emerge. Predictions as to bond angles can be made which are in agreement with those made by the theory of Pauling and Slater.

Further: the σ type of localized molecular orbital permits free rotation (single bonds), the π type, in double bonds, does not. This was first pointed out by Hückel. In triple bonds, however, (four π electrons), we again have free rotation. This explanation of the well-known absence of free rotation about double bonds, in terms of the properties of molecular orbitals, could have been paralleled in the theory of Pauling and Slater, if they had more freely used π in addition to σ (atomic) orbitals in forming electron-pair bonds. Actually, they suggested another explanation of the lack of free rotation; this, however, is applicable only to C = C bonds (not, for example, to N = N), and appears to be inadequate.

The nature of the method of non-localized molecular orbitals can be illustrated by applying it to the structure of the methane molecule, and comparing the results with those of the other methods. Using either atomic orbital electron-pair bonds (Slater and Pauling) or localized molecular orbital electron-pair bonds (Hund), there are four equivalent C-H bonds in CH_4, one for each H. In the Pauling-Slater method, each electron-pair is formed by one electron assigned to a 1s hydrogen atom orbital and one assigned to a "tetrahedral" carbon atom orbital which is obtained by mixing 2s and 2p carbon atom orbitals in a certain way. In Hund's method both electrons of a bond are assigned to a C-H-bonding localized molecular orbital of the σ type, which may be approximately represented by adding together a hydrogen atom 1s and a carbon atom tetrahedral orbital.

In the third method, using non-localized molecular orbitals, the electronic structure of CH_4 is described by assigning electrons to molecular orbitals of the CH_4 molecule-as-a-whole. The latter considerably resembles the isoelectronic atom neon in its high symmetry, chemical inertness, etc. In terms of orbitals, the neon atom has the structure

$$(1\underline{s})^2\ (2\underline{s})^2\ (2\underline{p})^6,\ {}^1\underline{S}.$$

Molecular orbitals of CH_4-as-a-whole are found to resemble the atomic orbitals 1<u>s</u>, 2<u>s</u>, and 2<u>p</u> of neon. The 1<u>s</u> orbital of CH_4 is essentially a carbon atom 1<u>s</u> orbital. The 2<u>s</u> orbital, spherically symmetrical in neon, is stretched out in methane so as to cover the four H nuclei. This modified 2<u>s</u>, or [2<u>s</u>], orbital is occupied by two electrons, like the 2*s* of neon. These two electrons wander about over the various regions of the [2*s*] orbital, but the form of the latter is such that it makes each electron spend a large part of its time in what may be called the bonding regions, between the C and the four H nuclei, one fourth of this time for each H. On the average, these electrons cause an attraction of all four H atoms toward the central C atom.

In a similar way, we have six electrons distributed among three [2*p*] molecular orbitals, each of which is similar to a 2*p* neon atom orbital, but stretched out in such a way as to cover the H nuclei. The [2*p*] electrons, like the [2*s*], spend a large part of their time in the bonding regions. The average effect of the two [2*s*] and six [2*p*] electrons is to produce a strong and symmetrical bonding between the C and the four H atoms.

This method of non-localized orbitals is particularly adapted to the description of the electronic structures of simple molecules and radicals RH_n, since the analogies of such molecules to the isoelectronic single atoms are rather strong. It can, however, be applied also to the shared electrons in molecules like CCl_4, CH_3Cl, C_2H_4, ClO_3^-, MnO_4^-, $PtCl_6^-$, $Cv(NH_3)_4^{++}$, and so on, but probably not very well to more complex types such as long-chain molecules. Even before its application to CH_4, however, Bloch used it for the solid state, and Hückel applied it to C_6H_6, later extending it to even more complex molecules like triphenylmethane.

Returning to the example of CH_4, the method has the advantage that it predicts directly that the valence electrons of CH_4 should have two quite different ionization potentials, one for [2*s*] and one for [2*p*], analogous to the 2s and 2p potentials of neon. An understanding of molecular ionization potentials is of interest not only directly, but also especially for an interpretation of electronic excited states and ultraviolet spectra, since the excited states are best thought of as formed by removing one electron, then putting it back in an excited orbital.

The same results can also be obtained by the other methods, but only in an indirect manner. For example, if one uses either of the two approximations for CH_4 using four equivalent electron-pair bonds, one begins by considering the removal of one electron from any one of the four electron-pairs, the ionization energy being the same for each. This suggests that there should be a single ionization potential for the valence electrons, which is not correct. The correct result is, however, obtainable by noting that the four equivalent states which result from removal of one electron from a bonding electron-pair are not true states of CH_4^+. The latter are obtained by forming certain quantum-mechanical combinations of these four tentative states; this yields two true electronic energy-levels of CH_4^+ (assuming for purposes of argument that CH_4^+ has the same symmetry as CH_4). Thus we finally get two ionization potentials, just as with the method of non-localized molecular orbitals.

The method of non-localized orbitals has the advantage of providing a simple scheme for surveying the electronic energy levels of molecules and their ions. At the same time it makes obvious the equivalence of the four C-H bonds, even though it describes them less simply than do the other two methods. The three methods probably all give fairly good approximations to the true electronic structure of CH_4. They should not necessarily be regarded as competitors, but rather as different directions of approach to the true structure of CH_4 which is, unfortunately, so complicated that it probably cannot be exactly described by any one simple method.

Remarks analogous to the preceding apply, on the whole, to polyatomic molecules in general. In the case of diatomic molecules, the three good approximations reduce to two, since there is no distinction between localized and non-localized molecular orbitals. The same two types of methods (atomic orbitals and molecular orbitals) are also available, in more or less generalized form, for substances in the solid state.

In conclusion, it should be mentioned that one of the advantages of the methods using atomic orbitals is that they are well adapted to approximate calculations of the energies of interaction between atoms. This is of value not only in dealing with stable molecules in their normal states, but also in predicting what happens when atoms collide and react chemically (energies of activation and rates of reaction). This latter field has been developed especially by Eyring and his collaborators. The methods using molecular orbitals, on the other hand, although probably not adapted to such calculations, appear in general to give simpler and more flexible ways of qualitatively describing chemical bonds for molecules of all types and all degrees of polarity, and to give a relatively simple scheme for dealing with the electron states and ultraviolet spectra of molecules.

THE NATURE OF CHEMICAL BINDING

PART II

Quantum Mechanics and Valence

G. W. Wheland*

Introduction

It has long been the aim of chemists to reach an adequate understanding of the nature of the forces responsible for valence bonds, but not until the last few years has any significant progress been made in this direction. The first important step was the formulation by G. N. Lewis of the theory of the shared electron-pair bond (1), which later received its full interpretation on the basis of the quantum mechanics in the work of Heitler and London (2), and of numerous subsequent investigators, The purpose of the present discussion will be to summarize the results of this development from the point of view which has been found particularly useful by workers in this laboratory.

The condition for the formulation of a valence bond between two atoms is that the energy of the system as a whole be lower for a configuration in which the atoms are close together than for one in which they are far apart. An understanding of the nature of the valence forces is accordingly to be gained from a consideration of the energy levels of atoms and of molecules. The Schrödinger equation (3), which embodies the fundamental postulates of quantum mechanics, states that

$$\underline{H}\,\psi = \underline{W}\,\psi \qquad (i)$$

where $\underline{W}$ is the constant energy of the system, ψ is a function of all the coordinates concerned in the problem, and $\underline{H}$ is the so-called Hamiltonian operator which can be readily set up for the individual case under considera-

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*Contribution from Gates Chemical Laobratory, California Institute of Technology No. 393.

tion, in accordance with definite rules outlined by Schrödinger. It is found, in general, that solutions, or eigenfunctions, ψ, which satisfy the necessary conditions of finiteness, continuity and single-valuedness, exist only if W takes on one of a usually discrete set of values, which are just the allowed energy levels of the system. If an eigenfunction, ψ_i, say, is known, the corresponding energy is readily obtained by multiplying the equation (i) by ψ_i^*, the complex conjugate of ψ_i, and integrating over the whole of configuration space. This gives

$$W = \frac{\int \psi_i^* \, H \psi_i \, d\tau}{\int \psi_i^* \, \psi_i \, d\tau} \tag{ii}$$

While ψ_0, the eigenfunction which corresponds to the ground state of the system, can always be found in principle by solving the wave equation (i), the mathematical difficulties involved in most cases of interest are so great in practice that recourse must be had to methods of approximation. Of these the most useful has been the variational method, which is based upon the fact that W_0 is a lower limit for expressions of the form given in equation (ii) (4). This means that if an approximate function is introduced into the integrals in place of ψ_0, the approximate value of W_0 thus obtained will be higher than the correct value, and that consequently the best approximation to ψ_0 is that which makes the expression for W_0 as small as possible. Slater (5) has outlined, in accordance with this principle, a general procedure for setting up approximate eigenfunctions for molecules with any desired structures. These are expressed as linear combinations of products of one-electron functions or orbitals which represent orbits about the individual nuclei, and which correspond to low-lying states of the atoms considered separately. The treatment is quite straightforward, but the resulting expressions are too involved to be given here.

Types of Bonds

There are found to be two extreme types of bonds, the ionic and the covalent. The former results from the ordinary electrostatic attraction of charged ions of opposite sign, and occurs in a number of molecules, of which NaCl may be considered a typical example. The latter results from a characteristic quantum mechanical effect which has no analogue in classical electrodynamics. If, for example, an approximate eigenfunction for a molecule in a given structure is set up in accordance with Slater's procedure, and if the approximate energy is then calculated from equation (ii), the resulting expression (neglecting the lack of orthogonality between orbitals on different atoms) is of the form:

$$W = Q + \sum (ab) - 0.5 \sum (cd) + \text{other terms} \qquad \text{(iii)}$$

where $a(j)$, $b(k)$, . . . represent the one-electron atomic functions, or orbitals, discussed above, expressed in terms of the coordinates of the j^{th}, k^{th}, ... electrons respectively; Q is the coulomb integral $\int a^*(1)b^*(2)c^*(3) \ldots e^*(n)Ha(1)b(2)c(3) \ldots e(n)d\tau$; (ab) is the single exchange integral $\int a^*(1)b^*(2)c^*(3) \ldots e^*(n)H\, b(1)a(2)c(3) \ldots e(n)d\tau$ between the orbitals a and b, the summation being taken over all pairs of orbitals united by covalent bonds; (cd) is the single exchange integral between the orbitals c and d, the summation being taken over all pairs of orbitals not united by covalent bonds, and the "other terms" include all the comparatively small multiple exchange integrals. Q usually has a small negative value, corresponding to a slight attraction between the atoms, but the chief contribution to the energy of the bonds comes from the exchange integrals (<u>ab</u>), which usually have fairly large negative values. The integrals (<u>cd</u>), on the other hand, give rise to repulsions between the non-bonded atoms, since they enter with negative coefficients. The justification for the rule of overlapping, which was established by Slater (6) and by Pauling (7) and which states that the most stable molecule is obtained when the bonded orbitals overlap as much as possible and the non-bonded orbitals as little as possible, lies in the fact that the absolute magnitude of the exchange integrals is roughly a measure of the overlapping of the corresponding orbitals.

Steric Factors

When the orbitals a, b. ... e. have been obtained by a treatment of the corresponding atomic problems, the functions which belong to the same nuclei are found to have steric relationships among themselves. The two bonding orbitals of the oxygen atom in H_2O, for example, have maximum values along axes which are approximately at right angles to each other. The rule of overlapping now demands that the two hydrogen atoms lie near these axes, and that the molecule have consequently a bent structure. Slater (6) and Pauling (7) have shown that reasoning of this type leads to a complete qualitative understanding of the factors determining the shapes of molecules in general, and also of the problems connected with rotation about single and double bonds.

Resonance

It has been mentioned that an eigenfunction, Φ_1, which represents a molecule with a given structure, is only approximate, and that, in accordance with the variational principle, the calculated energy is too high. A better eigenfunction can be written in the form

$$\chi = a_1\Phi_1 + a_2\Phi_2 + \ldots\ldots a_n\Phi_n \qquad \text{(iv)}$$

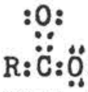
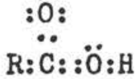
where Φ_2, Φ_3, ... Φ_n, are functions which represent further structures, and a_1, a_2 ... a_n are constants which are so chosen that the calculated energy is as low as possible. In many simple cases only one coefficient, a_j say, is of appreciable magnitude. Then χ is not very different from Φ_j, and the molecule can be described more or less adequately by means of the single corresponding structure. In other cases, several coefficients, a_j ... a_m say, may be of appreciable magnitude. Then χ is materially different from any single Φ, and the molecule can be described adequately only in terms of <u>all</u> the corresponding structures; the molecule is said not to possess a single electronic structure of the Lewis type, but to resonate among all those corresponding to the functions Φ_j .... Φ_m. Theoretical considerations show that the former state of affairs occurs in molecules in which one definite structure is considerably more stable than any others, while the latter occurs in molecules in which several structures are of nearly the same stability.

Determination of Bond Type

The complete theoretical determination of the types of bonds present in actual molecules is sometimes rather difficult, because of the laborious numerical calculations which are necessary before the relative stability of the various possible structures can be evaluated. For the practical solution of this problem, Pauling has developed three valuable methods which make use of the available empirical data. The following brief discussions will indicate the underlying principles of each, but for detailed descriptions, the reader is referred to the original literature.

(1). Ionization potentials and electron affinities (8). This criterion is of particular value in deciding whether a given bond is primarily ionic or primarily covalent, or resonates strongly between the two types. A superficial consideration is sufficient to show that the bond in NaCl, for example, is largely ionic, because the ionization potential of sodium is low, and the electron affinity of chlorine is high. The bond in H_2, on the other hand, is largely covalent, because the ionization potential of hydrogen is high, and its electron affinity is low. An intermediate case in which the bond partakes of both characters is represented by HCl.

(2). Atomic radii(9). Pauling has shown that the distance between two atoms united by a valence bond is the sum of the corresponding atomic radii, which depend only upon the nature of the atoms themselves and upon the type of bond involved. If a molecule resonates among various structures, each atomic distance is then approximately equal to the shortest calculated for any of the structures. For example, the observed moment of inertia of nitrous oxide corresponds to a triple bond distance between the two nitrogen atoms and a double bond distance between the nitrogen and the oxygen atoms. Consequently resonance between the two structures $:\ddot{N}::N::\ddot{O}:$ and $:N:::N:\underset{\cdot\cdot}{\ddot{O}}:$ is important, but the third structure $:\underset{\cdot\cdot}{\ddot{N}}:N:::O:$ makes no appreciable contribution, since otherwise both atomic distances would correspond to triple bonds, and the moment of inertia would be considerably smaller than the observed value.

(3). Bond and resonance energies. The energy of a molecule which can be represented adequately by means of a single structure is given fairly accurately by the sum of the energies of the individual bonds which it contains. Pauling and coworkers (10, 11) have calculated a number of such bond energies from empirical data, and have shown that within certain limits the values thus obtained are mutually consistent. The situation can be expected to be rather different, however, for molecules which cannot be represented by a single structure, since the complete eigenfunction must then be expressed as a combination of functions which represent the important structures. The energy is considerably lower as a result of this than would be calculated on the basis of any of the individual structures alone, and the molecule is stabilized thereby to a greater or less extent. Pauling and Sherman (11) have evaluated this extra "resonance energy" from thermochemical data for a number of typical cases, and have obtained valuable information regarding the structures of certain organic molecules. Thus, the carboxyl group is found to be stabilized to the extent of 1.2 electron volts (27.6 kg.-cal. per mole) by resonance between the two structures  $\mathrm{R{:}\overset{:O:}{\overset{::}{C}}{:}\underset{..}{\ddot{O}}{:}H}$ and  $\mathrm{R{:}\overset{:\ddot{O}:}{\overset{..}{C}}{::}\ddot{O}{:}H}$, and similar relations are observed in other systems. With the aid of these empirical bond and resonance energies it has been possible to interpret such chemical phenomena as: relative acid strengths of alcohols and carboxylic acids, relative basic strengths of amides and amines, equilibria in tautomeric systems (12), etc.

Theoretical calculations of resonance energies have been carried through by Pauling and Wheland (13) and by Pauling and Sherman (14) for a few types of molecules, and the results obtained in this manner have been found to be consistent with those obtained from thermochemical data. In benzene, for example, resonance between the two Kekulé structures,  and , stabilizes the molecule by 0.9 α, (where α is a single exchange integral between two adjacent carbon atoms in the ring), and resonance among the three equivalent Dewar structures of the form  contributes an additional 0.206 α. A comparison with the empirical resonance energy of 1.7 e.v. shows that $\alpha = -1.5$ e.v. In naphthalene, resonance among the forty-two possible structures produces a resonance energy of 2.015 α, and comparison with experiment in this case shows that $\alpha = -1,6$ e.v. Further calculations for a variety of additional molecules lead to similar consistent results. In particular, the dissociation of aryl substituted ethanes has been shown to be due to the extra stabilization of the free radicals by resonance to structures in which the unpaired electron is located on the ortho, para, etc. positions of the aromatic nuclei. The calculated dissociation constants are in fairly good agreement with experiment if α is put equal to -1.4 e.v.

Conclusion

In conclusion it may be said that in spite of the mathematical difficulties which have prevented complete quantitative treatments in most cases, the quantum mechanics has furnished a very satisfactory picture of the nature of valence. The point of view adopted in the present discussion has proved very useful in the interpretation of a wide variety of phenomena, but it is not the only one possible. Hund, Mulliken, and Hückel (15) have had similar success in attacking these same problems by a somewhat different method, and have interpreted the valence forces in a different way. The two points of view are complementary rather than antagonistic, however, and each has its own advantages in special fields.

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In the foregoing work of Mulliken and of Wheland we have a theoretical method opening up which sheds much light upon the fundamental problems of the structures of adsorption complexes and mechanism of lowering of energy of activation by catalysts. There is little doubt that this progress is real and not merely a glittering mirage in what e.g. to the organic chemist interested in catalysis is a dry and unknown desert of mathematics.

The Mechanism of Activation by Catalysis

We gain from quantum mechanics (a) a knowledge of what a bond is, (b) in principle a means for calculating the effect of neighboring atoms and forces upon that bond (1).

M. Polányi*, whose point of view takes full cognizance of the quantum mechanics, has been asked for his conception of the mechanism of activation by catalysts. The following is quoted from his letter, received January 5, 1934:

"I think it (chemical activation) is a process of rearrangement of the atoms into a state of transition which has equal chances to pass over into the final state or to return into the initial state. This rearrangement requires work, which appears as activation energy. Sometimes the energy of the transition can be calculated from the interaction of the homopolar valencies involved. In many cases, we have found recently that the energy is to be represented in an essentially different way. This is the case in ionic reactions and also when heteropolar compounds are formed in the reaction (2). I think that a number of other cases will be found in which the energy-expression will again be different.

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" . . . If in the presence of a third body a transition state can be formed, the energy of which is lower than the energy of the ordinary transition state, this body is acting as a catalyst. I think I have shown (3) that the splitting up of two molecules in such a way that the two halves form surface compounds with a solid gives a satisfactory model for homopolar surface catalysis of a reaction between those two molecules. I have there given reasons why the activation energy of the formation of the surface compounds might be small. H. S. Taylor has then pointed out that this is not always the case. Sometimes the formation of the surface compounds (activated adsorption) is accompanied by measurable activation energy. Balandin's work shows that the assumption of splitting up may hold true in some important cases (4).

"Perhaps it should be emphasized that though the chemists frequently have spoken of the splitting up of hydrogen on the catalyst as a reason for its activation, they have given no explanation whatever for the catalytic activity involved in the process. Such an explanation must at least show (1) why the splitting up is a quick process, (2) why the reactions of surface compounds are faster than those of ordinary molecules, (3) why desorption of the products should generally go quickly. To show this was the aim of my paper of 1929.

"Homogeneous? I do not feel quite hopeful on the subject, but I don't see that we have actually come any nearer to the subject than in its treatment by Lapworth, Lowry, Brönsted, Dawson.

"Of course, the energy of any transition state which has a higher electric moment than the initial and the final states must be lowered by the presence of ions, dipoles, or polarizable particles. It would be easy to sketch this out in general terms, but it is nothing substantial as yet."

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The above remarks of Polányi together with those in H. S. Taylor's contribution constitute a valuable summary of responsible opinion on the nature of activation by catalysts. The writer wishes to point out that concepts relative to this subject developed in the Sixth Report of the Committee on Contact Catalysis (5) do not require a very profound modification on account of the later developments.

The Nature of Active Centers

That catalytic surfaces are not necessarily uniform in their activity is to be concluded from the foregoing discussion, and represents a widely accepted view. The more active portions of the catalyst are called "active centers" although agreement as to their nature is by no means so general. The conceptions developed relative to the nature of activation provide for two factors which may contribute to the effectiveness of an active center (a) the nature of the available forces of the surface atoms, (b) the spacing of these atoms.

The possibility that both factors would be favorable in precipitated catalysts is evidently greater than for crystalline catalysts unless by rare chance the lattice dimensions in the latter case should be near the optimum. Not only is this true because of the various inter-particle distances in amorphous precipitates, but Taylor, Eyring and Sherman (1) find that minute crystals (which probably form the unit of structure in amorphous precipitates) may in general possess lattice dimensions differing widely from the normal.

On the whole the impression which may be gained from recent work relative to the nature of active centers does not differ substantially from that presented in the Sixth Report of the Committee on Contact Catalysis (5) except a possible special position of ions was neglected there.

Ions in Catalysis

It was pointed out under "General Considerations" that an important function of catalysts may be to relieve restraints on energy transfer, by providing a perturbation between systems otherwise relatively isolated. Ions would be especially effective for this purpose. Another type of catalytic action by ions is included in the above remarks by Polányi. A. K. Brewer, for some years has been suggesting that ions play a substantial part in catalysis. While his suggestions have not been pointedly connected with relief of energy transfer, in view of our new consciousness of this field of catalytic action, Brewer has been asked to summarize his evidence and has done so in what follows.

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Surface Ionization of Gases and Catalytic Activity

A. Keith Brewer*

In summarizing the effects of gases on the emission of ions from hot surfaces, Richardson (1) concludes that the result harmonizes with the view that the carriers are charged atoms or molecules of the gas liberated by its interaction with the metal. Recently these results have been extended by Brewer (2) who has attempted to correlate ion formation with surface catalysis.

The presence of adsorbed gas ions (adions) can be detected by measuring the change produced in the work function for electrons, and by an enhancement of the positive thermion current. An electron or ion in escaping from a conducting surface must do work against its electrostatic image attraction. This work is expressed by $300/4\ r^2$ volts per cm. (3); it becomes appreciable at 10^{-4} cm. from the surface and amounts to 36×10^6 volts at 10^{-7} cm. removed. The presence of positive adions tends to decrease the work function for electrons by counteracting the image field. A quantitative estimation of this decrease was obtained from measurements of the enhancement of the photoelectric emissivity from iron and tungsten surfaces on which a known amount of alkali ions had been deposited. The results showed that for small fractions of the surface covered the emissivity increases, and hence the work function decreases, in a manner nearly proportional to the fraction of the surface covered. The wave length vs. emissivity curves possess distinct characteristics for this type of composite surface; they show that the work function varies from point to point over the surfaces and that the field about the adion is appreciable to about

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ten times the ion radius.

Adsorbed gases, in specific cases, affect the photoelectric emissivity in exactly the same manner as do adsorbed alkali ions. To illustrate: the threshold of iron, normally about 2575 A, is shifted to 2750 A by H_2; to 2810 A by N_2; and to 4000 A by NH_3; but is unaffected by A. At 5 mm. NH_3 pressure the wave length vs. emissivity curves are identical to an iron surface 2% covered with K^+ ions, and show the same peculiarities characteristic of composite surfaces. The effect of various gases on platinum is distinctly different from iron; the threshold of 2650 A is unaffected by A, is shifted to 2750 A by N_2 and NH_3 and to above 3650 A by H_2. Thus NH_3 is highly dissociated on iron and only slightly on platinum, while just the opposite is true for hydrogen.

The dissociation of adsorbed gas into ions can be detected by an enhancement of the positive thermion emission as well as by the change in the photoelectric emissivity. It can be shown (3) from kinetic theory considerations that the number of adions escaping from 1 sq.cm. of surface per second is given by

$$N = n \sqrt{\frac{KT}{2\pi m}}\; e^{-m w_0^2/2kT} \qquad \text{(i)}$$

where $\underline{n}$ is the ion density at the surface, $\underline{k}$ is Boltzmen's constant, $\underline{m}$ the mass of the ion and $\underline{w}_0$ the velocity component an ion must have normal to the surface to just overcome the surface attraction. Since $0.5\,\underline{m}\,\underline{w}_0^2$ is work it may be replaced by $\underline{e}\,\phi$, where $\underline{e}$ is the charge on the ion and ϕ is the work function in volts. The positive ion current, therefore, is expressed by

$$i = \underline{n}\,\underline{AT}^{0.5}\,\underline{e}^{\frac{-e\phi}{kT}} = \underline{AT}^{0.5}\,\underline{e}^{-\underline{b}/\underline{T}}, \qquad \text{(ii)}$$

where <u>b</u> is Richardson's work function.

The results (2) from the positive thermion emission were in complete accord with those obtained photoelectrically. In the case of iron positive ions in the presence of NH_3 were detected at a lower temperature than from the best potassium impregnated emitters; N_2 had a more pronounced effect than did H_2. The results with nickel surfaces were similar to iron except that the effect of NH_3 was not quite as marked and that of H_2 was much more pronounced. Platinum on the other hand showed no effect from N_2 and a large effect from H_2; NH_3 showed a moderately small effect which came from the H_2 liberated from the small amount of NH_3 decomposed.

It is possible to correlate the above results with the catalytic activity of these surfaces as may be shown by the following examples. In the case of the decomposition of NH_3, iron and nickel are excellent catalysts and platinum is poor; NH_3 is markedly dissociated into ions on iron and nickel and not on platinum. Iron and nickel are good catalysts for NH_3 synthesis and platinum is poor; N_2 is appreciably ionized on iron and nickel surfaces while not on platinum -- the synthesis of ammonia is induced by N_2^+ ions but not by H_2^+ ions (4). On the other hand platinum is an excellent catalyst for the oxidation of H_2 while iron is comparatively poor; H_2 is dissociated into ions on platinum far more than on iron.-- the reaction is readily induced by H_2^+ ions (5).

If the chemical activity at a given surface is a function of the concentration of the ions initiating the reaction, then from equation (ii) the rate per unit volume can be expressed by

$$\frac{d\text{ɔ}}{dt} = n\ AT^{0.5}\ e^{-\frac{e\phi'}{KT}} \qquad \text{(iii)}$$

where $\underline{e}\,\phi$ is the work necessary to loosen the ions sufficiently from the surface for reaction to take place; $\underline{e}\,\phi$, therefore, is the chemical work function, and is identical to Q, the energy of activation in the ordinary expression for the rate of reaction. The fact that ϕ' for chemical action is smaller than ϕ for thermionic emission indicates that it is not necessary to remove the ion to any appreciable distance from the surface for reaction to take place.

In summary it has been shown by photoelectric and thermionic measurements that gases in specific cases are dissociated into ions upon adsorption by metallic surfaces; that there is a distinct correlation between the amount of dissociation and the possible catalytic activity; that the effect of temperature on the rate of ion emission and the rate of chemical action is expressed by the same form of equation; and that the values of the work function in these equations are in line with the concept that the chemical activity is dependent on ion formation.

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O. Schmidt (6) has suggested that catalytic hydrogenations proceed through the formation of ions in accordance with the schemes:

$$H_2 + 2\,\bar{e} = 2\,H^-$$

when the catalyst is an alkali or alkaline earth, and:

$$H_2 \longrightarrow H_2^* \longrightarrow H_2^+ + 2\,\bar{e} \longrightarrow H^+ + H$$

(H_2^* represents a deformed molecule)

when the catalyst is a metal of the variable valence type such as iron, platinum, copper, chromium, manganese and rhenium.

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INTERCHANGE OF ENERGY IN MOLECULAR COLLISIONS

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CONTENTS

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PART I

Interchange of energy between massive bodies.

Introduction

In many collisions between molecules and between molecules and surfaces the electronic structure of matter need not be considered. The atoms may be regarded as massive particles which attract, or repel, one another with a force depending only on their distances apart. It is with such collisions that the present section is concerned.

A naive model of a collision is one in which the atoms of each system are bound together by elastic forces, while the atoms of different systems interact as hard elastic spheres. The energy interchange may be calculated directly from the principles of conservation of energy and momentum provided only a single impact occurs during the collision. On this model it is possible to explain the persistence of the rotation of I_2, and the still greater persistence of the vibration of I_2, in He gas (1). In general more than one impact would occur according to this model, such as with the collision of an atom heavier than H with an H atom bound to a molecule. A calculation of the energy transfer on this model would then be very involved. Moreover, the calculation, if carried out, would give much too large an energy exchange. This is because the collision between two atoms is not instantaneous, but has a finite duration.

It has long been recognized that the finite time required to establish contact between two systems on collision acts as a severe restraint upon the change of the internal energy of the two systems. Thus if the contact between two solid rods took place instantaneously, their collision would in general be very inelastic (2). The observed high elasticity of such collisions is due, as Hertz (3) pointed out in 1882, to the roughness of the surfaces which makes the time taken in establishing a maximum contact longer than the time required for a sound wave to travel to and fro in the two rods. Jeans (4) (1903) has shown that the effect is even more pronounced in molecular collisions, and predicted that billions of collisions would be required to convert an appreciable fraction of vibrational energy into translational energy, or into vibrational energy of lower frequency. This is because the interaction between molecules is so gentle that in general many vibrations occur during the effective time of collision. The theory shows in fact that the energy transfer dies off exponentially with the number of these vibrations.

The simplest improvement upon the model of rigid spheres is the assumption that the atoms of separate systems repel one another according to some simple law. The law in vogue until recently was to take for the mutual potential energy V an inverse power of the interatomic distance, $\underline{Cr}^{-\underline{n}}$ (5). This law is unsatisfactory because of the lack of a theoretical justification, and because not only is the exponent $\underline{n}$ difficult to determine uniquely, but the best value of $\underline{n}$ varies from gas to gas. The repulsive law, $V = \underline{Ce}^{-\underline{r}/\underline{d}}$, is more plausible since at large distances the charge distribution about an atom dies off exponentially. Moreover, the quantity $\underline{d}$ is fairly constant from atom to atom, as may be seen from Table I.

TABLE I (6)

Values of $d(\times 10^8)$

	F	Cl	Br	I
Li	0.357	0.382	0.382	(0.460)
Na		0.326	0.334	0.384
K	0.319	0.316	0.326	0.351
Rb		0.356	0.340	0.351
Cs		0.310	0.327	0.355

The classical mechanics has predicted correctly, as we have seen, that, for $\underline{d}$ not too small, the energy of a rapid oscillator has an extreme reluctance to be transferred to a less rapid oscillator, or to translational degrees of freedom. For the actual calculation of the energy transfer, however, we must use quantum mechanics. The quantum numbers of the internal vibrations are usually small, so that the molecules have some essentially nonclassical properties. In particular, we cannot specify the phase of the oscillators.

The rotational quantum numbers of molecules are generally large, so we may specify the phase of the rotational coordinates at the beginning of a collision. Thus if we wish to find the energy transferred from the vibration of a diatomic molecule A to the rotation of a diatomic molecule B, we specify the initial phases as in Fig. 1.

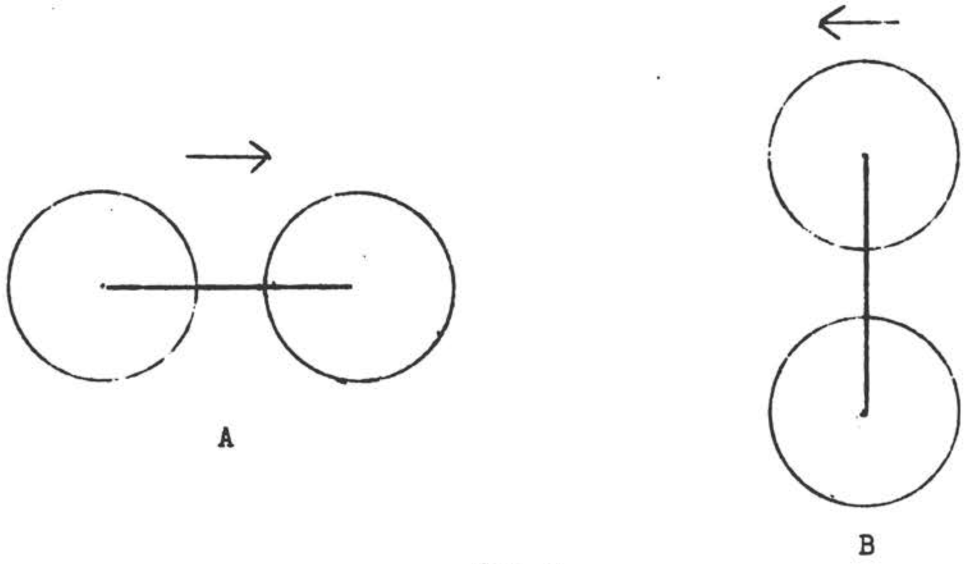


Fig. 1
Change of Rotational Energy.

In the case illustrated the energy transfer will be essentially the same as if the collision were between the molecule A and a free atom. H_2 is an exception. Its low rotational quantum number at ordinary temperatures prevents us from specifying the phase of its rotational coordinate. Here the rotation quantum number must be treated as an internal quantum number. The large energy which is absorbed by a change of rotational quantum number (the rotational quantum number must change by an even number, since para-H_2 remains para-H_2, and ortho-H_2 remains ortho-H_2) gives H_2 unique powers as a catalyst. In Table II we give for future reference the energy quanta which can be absorbed.

TABLE II

Rotational quanta absorbed by H_2

Quantum number j	0	1	2	3	4	5
Fraction of molecules in state j.	0.24	0.39	0.27	0.104	0.023	0.004
$E_{j+2} - E_j$ in electron volts.	0.042	0.070	0.10	0.13	0.15	0.18

We now consider the probability of a particular inelastic collision. Let one or more internal quantum numbers change, the total loss of internal energy being $\underline{h}\nu$. If the initial relative kinetic energy is ϵ, the final energy is then $\epsilon + \underline{h}\nu$. The probability $\underline{P}$ of this particular inelastic collision may be expressed as a product of factors (7), the first factor being a function of ϵ, $\underline{h}\nu$, and the reduced mass of the two systems, while each succeeding factor is associated with the change of only one internal quantum number. Thus

$$\underline{P} = \gamma(\epsilon)\, p_1 \, p_2 \, p_2 \cdots \qquad \text{(i)}$$

Except in experiments with molecular beams, we know only the distribution for the initial relative kinetic energy ϵ, i.e., only the temperature is given. Since the probability of an inelastic collision is very dependent upon the time of collision, and hence upon ε, the average value of $\gamma(\varepsilon)$ is, in general, of a different order of magnitude from the value of $\gamma(\varepsilon)$ for the average value of ε. The average value of $\gamma(\varepsilon)$, $[\gamma]$, is given in Fig. 2 (8). If we wish the average value of γ when the internal coordinates absorb instead of lose the net energy $h\nu$, we have merely to multiply $[\gamma]$ as given in Fig. 2, by $\exp(-h\nu/kt)$.

In a collision involving H_2 one factor p may be associated with the change of rotational quantum number of H_2. In all other cases each factor p is associated with a particular normal coordinate of vibration which gains or loses energy. When a vibration quantum number changes from $n - 1$ to n, or from n to $n - 1$, the corresponding p is given by the equation

$$p = n(\beta s/d)^2 \tag{11}$$

The quantity β represents the coupling of the normal coordinate with the atom which suffers the impact during the collision. Thus if we expand the displacement of this atom from its position of equilibrium (with respect to its axis rotating with the molecule) in terms of the normal coordinates of the molecule, β will be the coefficient of the normal coordinate in question. Thus in a diatomic molecule $\beta = 0.5$. In the collision of an atom with a solid surface, we regard the solid as a cube having say M atoms. The $\beta = M^{-0.5}$ for such normal coordinates of the solid as correspond to a displacement normal to the surface. When we then sum over all transition probabilities, the factor M^{-1} vanishes. The quantity s is the matrix element of the normal coordinate with respect to the normal and first excited

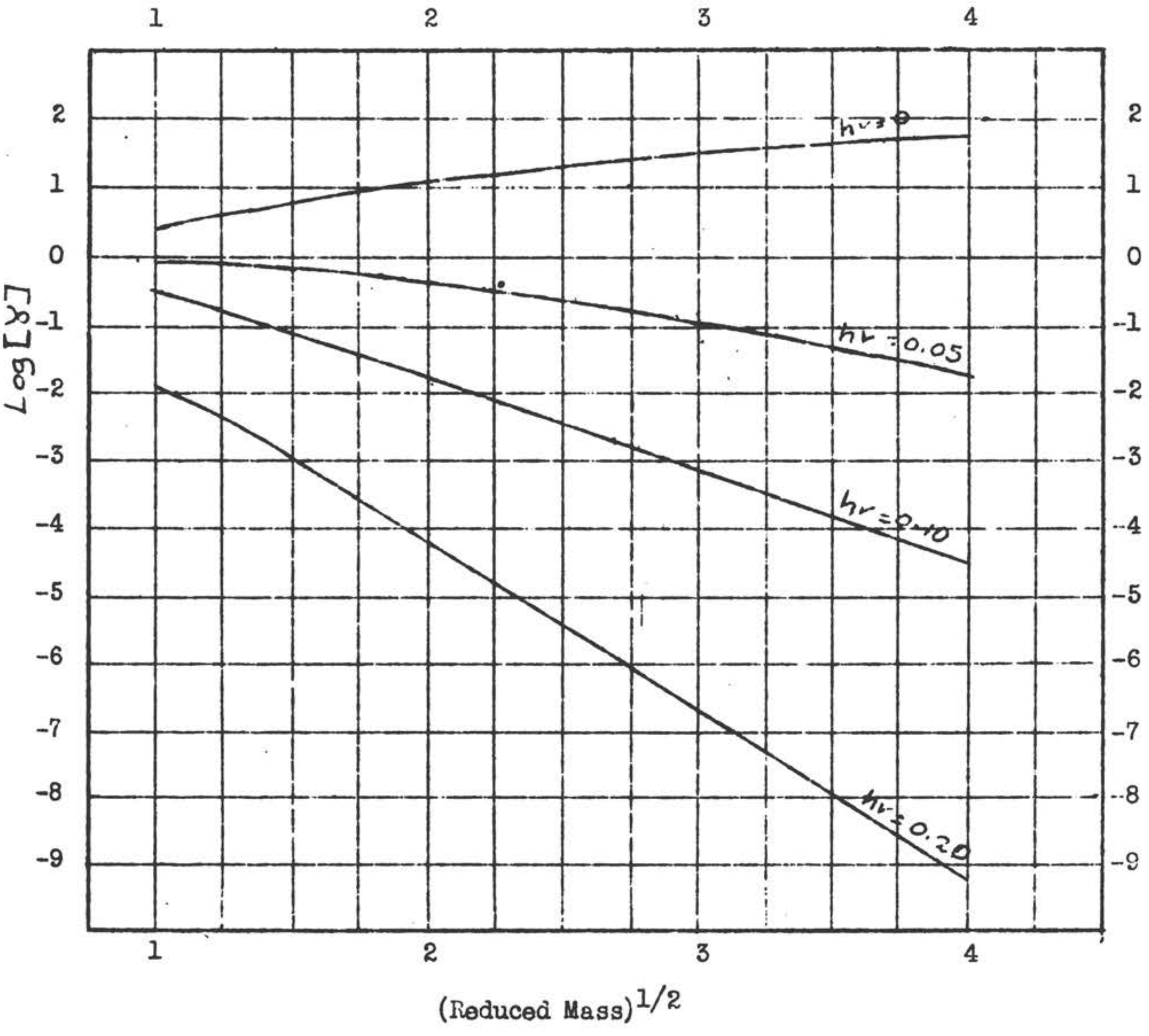


Fig. 2

Average value of γ, calculated for 300°K, with d - 0.35 x 10^{-8} cm. Mass is in units of atomic H, hν is in units of electron volts.

states. It is given by the equation (9)

$$s = (h/2m\nu)^{0.5}/2\pi \qquad \text{(iii)}$$

where m is the mass, and ν is the frequency associated with the particular normal coordinate. Typical values of s are given in Table III. The length d may be taken to be 0.35×10^{-8} cms. The factor associated with a change of the quantum number by more than unity is much smaller. Thus the factor for the transition $n = 0$ to $n = m$ is equal to the m'th power of the factor for the transition from $n = 0$ to $n = 1$.

Before we can give the value of p which is associated with a change in the rotational quantum number of H_2, we must know the dependence of the interaction energy upon the angle θ from the nuclear axis. A reasonable dependence is $\cos^2\theta$. Then the factor p for a change of two units is 1/4, and zero for other changes.

As an example of equation (i), we calculate the average probability of an inelastic collision between a He atom and an O_2 molecule in the first excited state. Here the reduced mass is about $4M_H$, and $h\nu = 0.23$ electron volts, so from Fig. 2 we obtain $[\gamma] = 10^{-5}$. From equation (ii) and

TABLE III

Values of $x \times 10^8$

H_2	N_2	O_2	C - C	W (solid)*
0.040	0.017	0.017	0.019	0.019

* s of normal coordinate of highest frequency.

Table III we obtain, using $\beta = 1/2$, $\underline{p} = 6 \times 10^{-4}$. We thus have

$$[\underline{P}] = 6 \times 10^{-9}$$

We are now in a position to examine more closely the restraint which the gentleness of the collision has upon the transfer of energy. In the first place let the lack of resonance $\underline{h}\nu$ be zero. The probability that an energy quantum is transferred from a normal coordinate of one molecule to the normal coordinate of a second molecule is proportional to $\underline{d}^{-4}$. For the particular case of the transfer between, say, two N_2 molecules we obtain for the probability average $\underline{P}$ the value $[\gamma]$ $\underline{p}^2 = 40 \times (6 \times 10^{-4})^2 \simeq 10^{-5}$. When $\underline{h}\nu$ is different from zero the restraint is much more severe. It is the more important the heavier the molecules (cf. Fig. 2), for then the relative velocity is lower, and hence the time of collision is increased.

Equation (i) will give a probability greater than unity when the reduced mass is large and when $\underline{h}\nu$ is sufficiently small. The assumption under which this equation was derived is of course then no longer valid. In such a case the probability will be less than but comparable to unity.

Anomalies in Sound Propagation

The reluctance of the internal energy of molecules to be converted into translational energy may have a profound effect upon the propagation of sound in polyatomic gases (10). As a sound wave passes, the periodic expansion and contraction of the gas is accompanied by a periodic change in the temperature. Now if the period of the sound wave, $1/\nu_s$, is much shorter than the time τ required for equilibrium to be established between the translational energy and the internal energy (assuming only one internal vibrator) the internal energy will not follow the fluctuations, and hence will not contribute to the effective specific heat. Conversely if $1/\nu \gg \tau$, then the specific heat associated with the vibrator will have its normal value. The velocity of sound will have different constant values in the two regions. In the transition region the velocity will vary with the frequency, and the energy of the sound wave will be dissipated. Gas molecules with more than one vibrator will have a transition region associated with each vibrator.

The time τ required to establish equilibrium is roughly equal to the time required for a quantum of vibration to be converted into translational energy. From equation (i), Table II, and Fig. 2, we see that for O_2 τ is of the order of seconds ($h\nu$ = 0.23 electron volts, number of collisions $\simeq 10^{10}$ sec^{-1}), Hence equilibrium cannot be established by O_2 molecules alone. Certain gases may, however, act as *catalysts* for maintaining equilibrium. If such a catalyst is to transform vibrational energy into translational energy in a single collision it must be very light [*cf*. Fig. 2 (H_2, He?)]. Or the catalyst must be able to absorb nearly the whole $h\nu$ as internal energy and then dissipate this energy as translational energy in smaller quanta. We see from Fig. 2 that internal energy will be dissipated much more rapidly if it can be given up to translational energy as several small quanta than as one large quantum. Knudsen (11) has found that water molecules act as such a catalyst.

The smaller $h\nu$ of CO_2 and H_2O allow equilibrium to be established without the aid of catalysts, although water has been found to hasten the equilibrium. The experimental results are given in Table IV in terms of the number of collisions necessary to dissipate an internal quantum of vibration.

TABLE IV

Number of collisions necessary to dissipate one vibrational quantum. Experimental.

	CO_2 (0.084)*	H_2O (0.17)	O_2 (0.23)	N_2 (0.35)
Collisions with like molecules	5×10^4 (12)	5×10^3 (13)	10^{12}**	10^{12}**
Collisions with H_2O	$200^{(14)}$		10^4 (15)	

*Numbers in brackets are the energy quanta $h\nu$ in electron volts.

**Calculated.

It is interesting to note the much greater effectiveness of the collision of H_2O with CO_2 than with O_2. This is probably due to the greater difficulty of H_2O in absorbing a large quantum of 0.23 electron volts.

Unimolecular Dissociation

A study of unimolecular reactions yields interesting information about changes in the internal energy of molecules during collisions. Complex molecules dissociate with a unimolecular rate when the natural life of the activated molecules is much longer than the time between deactivating collisions (16). Of particular interest is the fact that H_2 alone of all foreign gases (except gases of similar nature to the dissociating gas) is able to deactivate the molecules (17). Moreover, a molecule of H_2 is about as effective as a molecule of the dissociating gas.

We shall not investigate what information the theoretical considerations of the above introduction yield upon this problem. Following Rice (18), we shall take as a typical deactivating collision one in which an oscillator of frequency $\underline{h}\nu' = 0.125$ electron volts goes from the fourth to the third quantum level. When the deactivating molecule is of the same kind as the activated molecule, except that its oscillators are in their normal state, we obtain $[\gamma] \simeq 10^2$, and $\underline{p} = 6 \times 10^{-2}$ and 1.5×10^{-2} for the activated and the deactivating molecule respectively. We have omitted the factors β, as in the most favourable case they will disappear when we sum over all the normal coordinates of both molecules. In this case we thus obtain the average deactivating probability $\underline{P} \doteq 0.06$. We shall now calculate the efficiency of H_2, assuming the energy to be mostly absorbed as rotational energy. Assuming that on the average 0.025 electron volts (<u>cf</u>. Table II) must be absorbed as translational energy due to lack of resonance, we obtain $[\nu] = 5$, and $\underline{p} = 6 \times 10^{-2}$, 0.25 for the activated molecule and for the H_2 molecule, respectively. This gives the same efficiency as before, namely 0.04. We now calculate the efficiency of the deactivating collisions when all the energy $\underline{h}\nu$ must go into translational energy. We have $[\gamma] = 0.016$ or 0.006, according to whether the deactivating molecule is H_2 or He, and the $\underline{p}$ for the activated molecule is the same as before. We obtain for the efficiency 0.001, 0.0004 for H_2, He, respectively. The efficiency of any heavier gas will be much less (<u>cf</u>. Fig. 2).

We thus conclude that the comparatively large quanta which H_2 can absorb as internal energy of rotation makes it unique in deactivating efficiency. We also see the efficiency for deactivation by like molecules may be considerably less than unity, as is sometimes observed (19).

Energy Interchange between Atoms and Solid Surfaces.

The interchange of energy between solid surfaces and a gas is obtained experimentally by the cooling effect of the gas. The energy interchange with the light gases, H_2 and He, is of most interest, since other gases are in general first absorbed and then re-emitted (20).

If $\underline{T}$ is the temperature of the surface, and $\underline{t}_1$, $\underline{t}_2$ are the temperatures of the gas atoms before and after collision, then the energy interchange is measured by the <u>accommodation</u> coefficient.

$$\alpha = \underline{t}_2 - \underline{t}_1 \; / \; \underline{T} - \underline{t}_1$$

The only measurements of α using clean surfaces are those of Roberts (21), with He and W. His values are shown in Fig. 3(See Page 117). These low values of α are due to several causes. In order to examine these effects separately it is best to consider only collisions of the type shown in Fig. 4 (See Page 117). Double collisions are thus avoided. We isolate the effect of the small ratio of the masses of He and W by regarding the gas and surface atoms as hard elastic spheres, and by letting the surface atoms be bound to their positions of equilibrium by such small forces that their energy quanta $\underline{h}\nu$ are much smaller than $\underline{kt}$. Then (22)

$$\alpha = 4 \; \underline{m}_{He} / \underline{m}_{W} = 0.087$$

and would be again raised by double collisions.

The primary effect of the quantisation of energy, $\underline{h}\nu > \underline{kT}$, is to introduce a dependençe upon the temperature. This is given approximately by the factor

$$\text{energy content per atom of solid} / \underline{kt} \;;$$

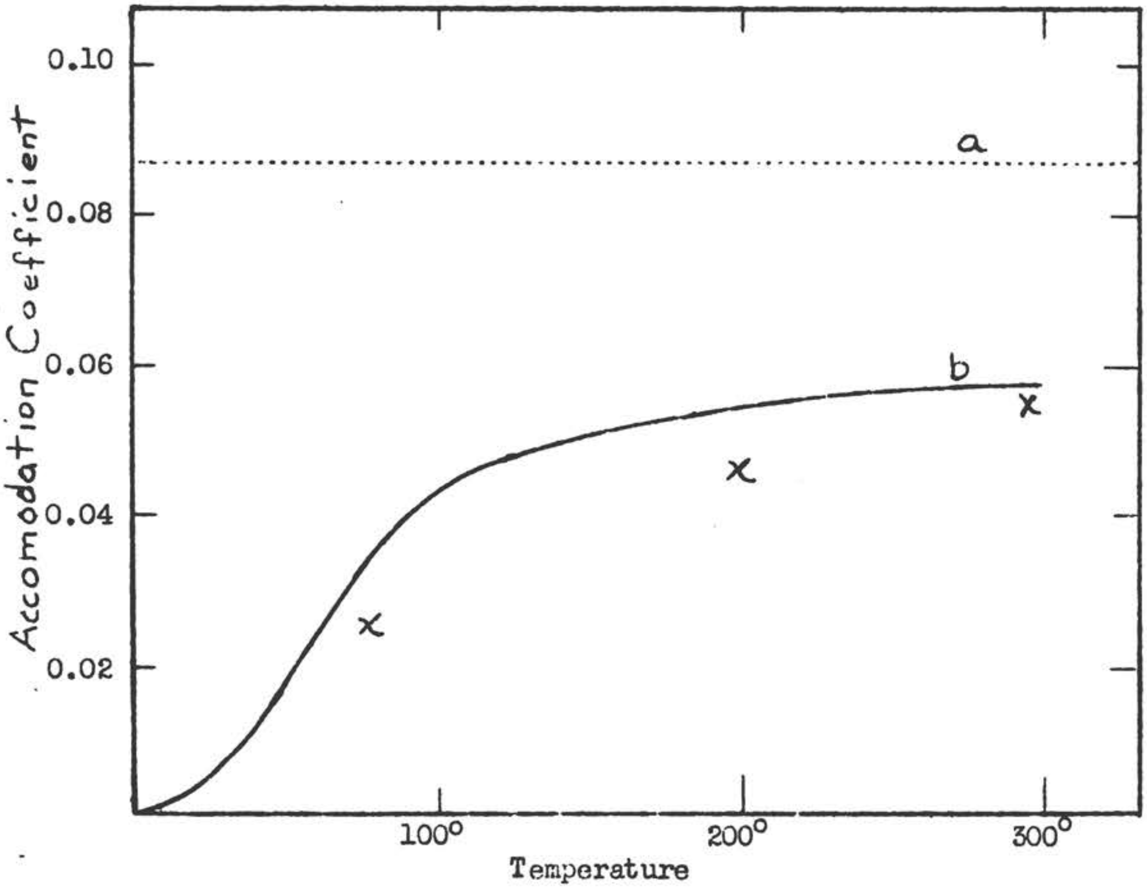
this effect thus makes α approach zero at the absolute zero temperature (no attractive forces between He and surface being assumed). It is readily seen how the small specific heat of the solid at low temperatures will reduce the amount of energy transferred.

Finally, there is the effect of the gentleness of the repulsive forces between the gas atoms and the surface, which was discussed in the Introduction. The effect will be quite different according to whether we regard the surface atoms as bound to positions of equilibrium, as in the Einstein theory of specific heats, or treat the motion by the normal coordinates of the solid as in the Debye theory of specific heats. For we say in the Introduction that the restraint upon the exchange of energy between an atom and an oscillator depends upon the ratio of the time of collision to the period of the oscillator. This restraint is thus much more severe for the normal modes of vibration with high frequency, which are the only ones present in the first model.

Although the small energy interchange between He and a W surface is, aside from the temperature dependence, essentially a classical effect, the high per cent <u>elastic</u> reflection of light atoms from surfaces is a distinct quantum phenomenon. Only the atoms reflected elastically (no energy interchange with the surface) can give de Broglie diffraction patterns. Such diffraction patterns have been observed for H and He atoms with crystals

Fig. 3

X experimental points. Curve (a); α for no energy quantisation. Curve (b): Debye function, U/kt, times an arbitrary constant.



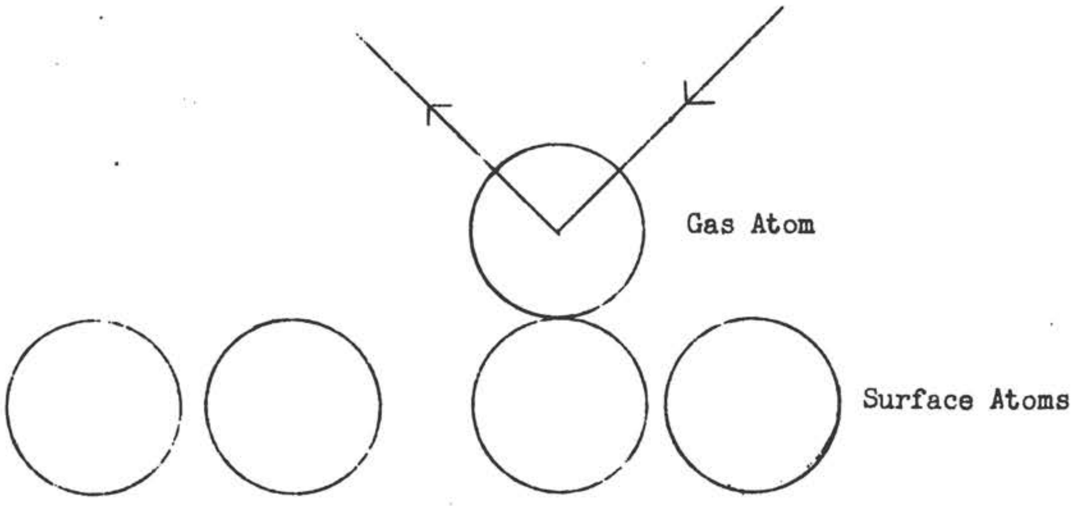


Fig. 4

Model of a collision of an atom with a solid surface. Only the normal component of the velocity of atoms is changed.

of LiF, NaCl, etc. (23). According to the classical mechanics some energy would always be either gained or lost in a collision. This is not true in quantum mechanics, there being a probability not much less than unity that no energy transfer occurs during the collision (24). This difference between the two mechanics is best seen by considering a single linear oscillator acted upon by a small external force between the times $\underline{t}_0$ and $\underline{t}_1$. The calculation of the energy change of the oscillator is the same whether performed according to the classical or quantum mechanics, provided, in the first case, that we average over all initial phases of the oscillator. However, according to the classical mechanics the probability is infinitesimal that the energy be the same after the application of the force as before, while this probability is finite in the quantum mechanics.

PART II

Interchange of Electronic Energy

The interchange of electronic energy between two systems is very improbable unless the electronic energy given up by one system can be almost all absorbed as electronic energy by the second system. In such a case the energy interchange has a probability of 1/2 if the closest distance of approach of the two systems, $\underline{p}$, is less than a critical value $\underline{p}_0$ (25). As $\underline{p}$ becomes greater than $\underline{p}_0$, the probability vanishes very rapidly. The effective cross section for the transition is thus equal to $\pi \underline{p}_0^2/2$. The case where both systems are isolated atoms, and the transitions are optically allowed, has been thoroughly investigated. The effective cross section is shown in Fig. 5 (See Page 119) as a function of the energy σ

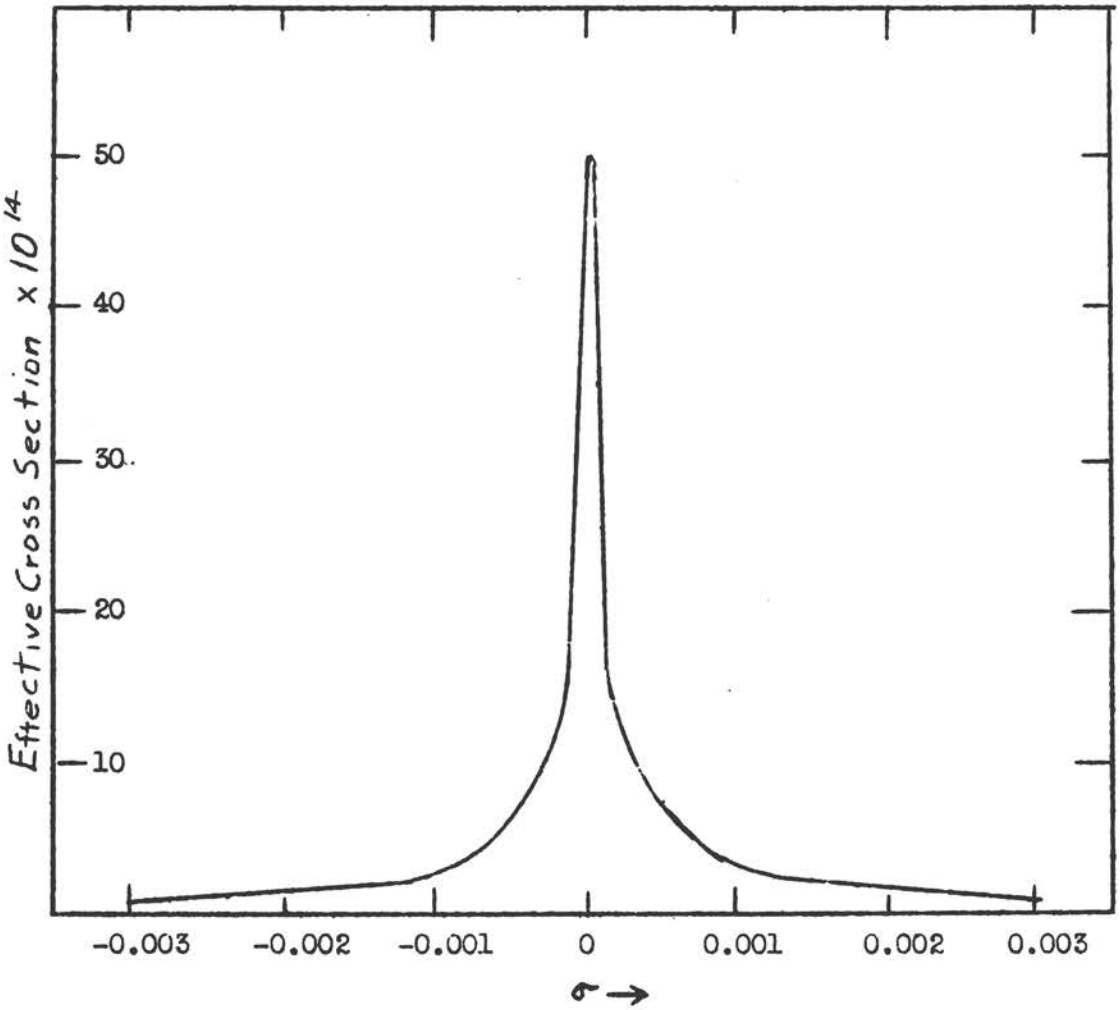


Fig. 5

Effective cross section for optically allowed transitions at room temperature. The effective dipole moment of each atom has been taken as $\underline{e} \times 10^{-8}$. σ is in units of electron volts.

which must be absorbed as translational energy. Other types of transition have been studied (26), but no general results can be given.

The writer wishes to stress that the extremely sharp resonance shown in Fig. 5 is not peculiar to the quantum mechanics. Exactly the same curve is obtained if we replace each atom by a system of virtual oscillators and calculate (27) on the classical mechanics the effective cross section for the energy transfer from an excited to a non-excited virtual oscillator in a different atom. Then of course $\sigma = \underline{h}\nu$, where ν is the frequency difference of the two oscillators. In the literature this sharp resonance is often spoken of as a pure quantum phenomenon.

PART III

Interchange of Energy between Electrons and Massive Bodies

In Part II we examined a case where a change of electronic quantum numbers is accompanied by a very small change in the translational energy of two colliding systems. However, the collision of two systems is in general accompanied by a large change, at least a transitory change, in the kinetic energy of the massive bodies, even when the electronic quantum states remain unaltered.

Since the electronic motion is much faster than the motion of the atoms, it is customary to regard the atoms as interacting with a mutual potential energy, this potential energy being, aside from the coulomb interaction between the nuclei, the total energy which the electrons would have if the atoms were stationary. The potential energy diagram of a diatomic molecule is a familiar example. A trivial example of the interchange of energy between electrons and massive particles is thus the vibration of a diatomic molecule.

Interesting conclusions may be obtained when we consider the potential energy as a function of two parameters. Thus take the collision of an excited Hg atom with a hydrogen molecule, the two parameters being indicated in Fig. 6. If we let x and y be rectilinear coordinates, and plot the potential energy

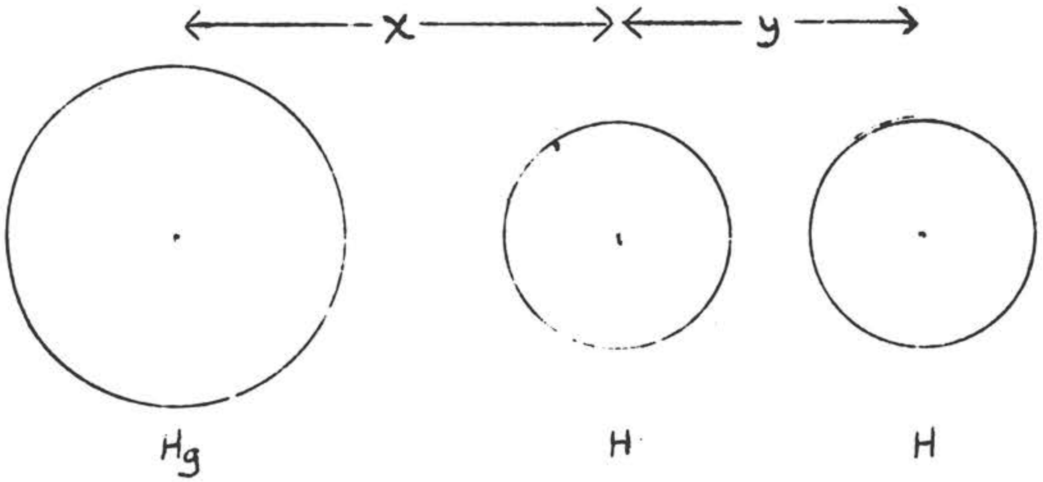


Fig. 6
Model of collision of excited Hg atom with
H_2 molecule.

along the z axis, we obtain a potential energy surface. This surface will have two valleys, one parallel to the y axis for large values of y, and one parallel to the x axis for large values of x. These two valleys represent the systems normal HgH + H, excited Hg + H_2, respectively. Since the first valley is deeper than the second, the collision of excited Hg with H_2 may be accompanied by the formation of HgH + H, the hydrogen atoms after the collision having a large amount of kinetic energy which has been obtained from the electronic energy of the excited Hg atom. This method has been used extensively by Eyring and his collaborators in studying chemical reactions (28).

If the parameters of a system move sufficiently rapidly past a region where two potential energy surfaces come close together the electronic quantum state will change, so that the system will pass from one potential energy surface to another. The one dimensional case has received special study (29). It is illustrated in Fig. 7.

The transition probability is $\exp\left\{-\frac{\pi^2 \varepsilon^2}{h v \left| s_1 - s_2 \right|}\right\}$

where ε is the smallest distance between the two potential energy curves, v is the velocity $\left| dR/dt \right|$, and s_1, s_2 are the slopes of the asymptotes to the two potential energy curves.

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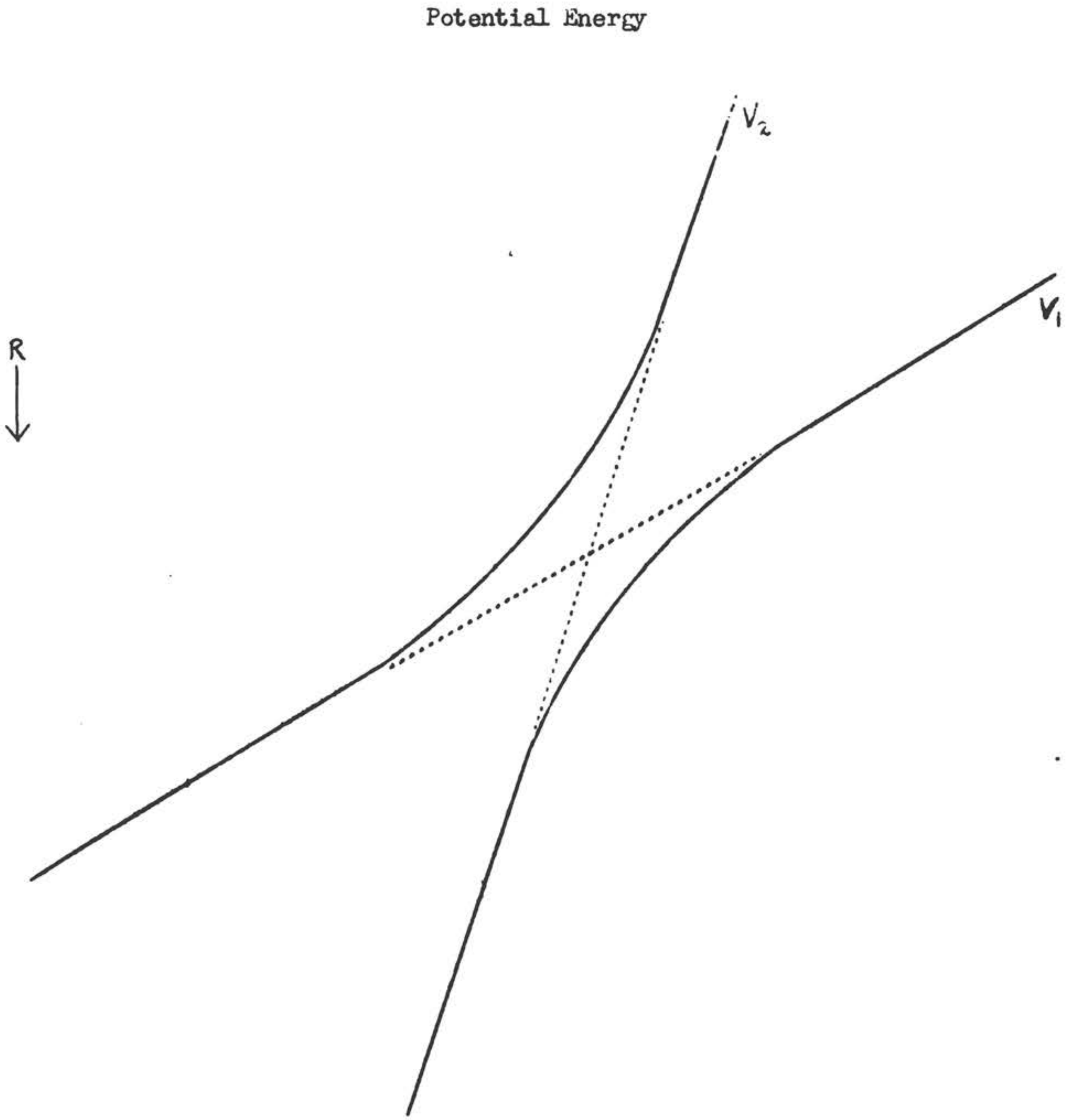

Fig. 7

Non-adiabatic crossing of energy levels.

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CHAIN REACTIONS AND INHIBITORS

In the simple cases of chemical reaction, one set of properly activated reactent molecules react to give the stoichiometric set of product molecules and further reaction must wait for additional active molecules to be created through the normal processes of energy distribution. But it may also happen that, during the reaction, bodies are generated which increase the rate at which active molecules form. These reactions are very different kinetically from the simple types and are called chain reactions. These bodies are evidently in a sense catalysts. They may be (a) merely product molecules of high energy content (in the case of exothermic reactions) (1), (b) radicles or atoms (2) as illustrated by

$$H_2 + O_2 \longrightarrow 2\,OH$$

$$OH + H_2 \dashrightarrow H_2O + H \text{ etc.}$$

(c) orthodox molecules which act as catalysts but are themselves destroyed after a short life. This is illustrated by the peroxide theory (3) of the oxidation of hydrocarbons.

The field of chain reactions has been reviewed by Semenoff (4) and more recently by Hinshelwood (5), both of whom have contributed extensively to the field.

Milas (6) has collected 273 papers on the subject of autoxidation, perhaps the most prominent example of chain reactions. His point of view, however, is not the kinetic one.

Not only are chain reactions particularly sensitive to catalysts which may act in the sense of a trigger, but they are often susceptible to inhibition. A theory of inhibition based upon the first type (a) of chain reaction was put forward by Christiansen (7), and received a substantial following induced partly by the experimental work of Bäckström (8). According to this theory an inhibitor acts by taking selectively the energy from the product molecules in such a way that this energy becomes ineffective in activating fresh reactant molecules.

The thermal chain theory itself indisputably represents a possible contributing factor in some cases. It would be most probable when reactant and product molecules are small, in the early stages of a strongly exothermic arrangement reaction in the gas phase at low pressure. Departures from these ideal conditions render the mechanism less and less probable the greater the departure. Thus if the molecules are large, they act as reservoirs for the storage of energy of reaction and activation so that the certain selective transference of this energy to a fresh reactant molecule becomes improbable and the certain reaction of this large reactant molecule even if activated by such a procedure itself becomes improbable. As cold product molecules pile up the chance for the dissipation of energy of reaction and activation to them rather than to fresh reactants increases. In solution the molecules of solvent also would act as acceptors for this energy. For reactions involving more than one product molecule, there is distribution of energy in the act of reaction itself. For the proposed mechanism of inhibitor action to obtain, one then has to assume that it is very specific in its ability to take up the energy from energized products even when compared with the corresponding power of reactant molecules, and that it is then unable to give up the energy in such a way as to activate fresh reactants with high probability.

The writer (9) feels that this compounding of probabilities renders the thermal chain interpretation of inhibition of reactions as a general mechanism a little too much to expect of one's credulity. Moreover, inhibitors are effective in preventing the oxidation of rubber which would seem to offer a superlatively inappropriate setting for a chain mechanism.

Bäckström's "proof" of a mechanism of inhibition consisted in setting up a general parallelism between the influence of inhibitors on the dark and light reactions for certain oxidation reactions, the latter having been shown from quantum efficiency measurements to be of the chain type. There were, however, various irregularities in Bäckström's proof, e.g., when a sodium sulfite solution was illuminated with line 265, the reaction with oxygen proceeded after the light was turned off at a rate not sensibly lower than the rate in the light indicating the formation of catalytic bodies, since line 254 was as effective but did not give rise to a photochemical after effect anything like as great (10). In other cases (11) the quantum efficiency for the light reaction varied with light intensity. Worst of all for his argument, there are cases (12) when an inhibitor affects the light reaction without affecting the dark reaction and vice versa.

More recently quite different interpretations of some of the reactions investigated by Bäckström have appeared. Thus Franck and Haber (13) suggest that in the autoxidation of sodium sulfite solutions, the chains are not thermal but are propagated by means of atoms or radicals. In their mechanism, the known powerful catalytic action of cupric ions is likewise taken into account.

Bodenstein (14) too suggests that in the oxidation of hydrocarbons and aldehydes, more or less stable intermediates structurally, not merely energetically, different from product molecules are formed in the process.

Various other factors may be advanced against thermal chains in many practical cases. Thus some oxidation reactions (15) are thought to start at surfaces, whereas highly energized product molecules would be expected to lose that energy to the surface and leave it with average energy corresponding to the temperature of the system. According to Raymond (16) benzaldehyde when sufficiently pure does not react with oxygen at ordinary temperatures.

The writer feels in view of the foregoing and other considerations that the chance of the thermal chain mechanism and therefore the Christiansen theory of negative catalysis applying very generally in their original form is remote. A firm decision in the matter depends among other things upon the quantitative values which may be given to the probabilities of energy exchange in various cases.

The state of knowledge in this respect is set forth on page 103 in this report by C. Zener.

If one limits probable general chain mechanisms to (b) and (c) above, and then revises Christiansen's theory of inhibition accordingly, the writer would concur in the attitude. It should be remarked, however, that the theory of inhibition would then become substantially the same as the original one, i.e., that an inhibitor acts by preventing the action of a positive catalyst (17). The difficulty of determining the precise mechanisms in such cases should also be reiterated.

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Homogeneous Catalysis

While a huge number of papers have appeared upon the subject of catalysis in solution, until recently no examples of homogeneous catalysis in the gas phase have been subjected to kinetic study because the choice of a suitable example was a matter of discovery rather than selection. Thus the writer and G. J. North (1) attempted to study the gaseous reaction

$$SO_2 + NO_2 = NO + SO_3$$

catalyzed by water vapor. Unfortunately the reaction appeared to be largely heterogeneous.

Hinshelwood and Glass (2) discovered that iodine had a pronounced catalytic effect upon the thermal decomposition of isopropyl ether and that the catalytic reaction was homogeneous. Subsequent investigations (3) disclosed that certain types of compounds: aliphatic ethers (except dimethyl), aldehydes, aliphatic amines (except methyl amines and mono amines), and esters were catalyzed. Ketones, alcohols, alkyl halides, carboxylic acids, and paraffins are thought not to be catalyzed.

The reactions all consist of the migration of a hydrogen atom and the breaking of a bond which possesses a dipole moment. They are characterized by a simplified activation mechanism. The catalyst is the iodine molecule rather than the iodine atom. In the catalyzed decomposition of diisopropyl ether only two square terms need be taken into account, that is the number of collisions between iodine molecules and ether molecules is the total number of collisions multiplied by $e^{-E/RT}$. E in all these cases has a much lower value than for the uncatalyzed reaction.

It is concluded that the polar nature of the bond which is broken together with the polarizability of the iodine molecule make for a facilitation and simplification of energy transfer to that particular point. The bond in question is likewise thought to be weakened by the iodine. The explanation is in part thought to be an increase in the perturbation factor required by quantum mechanics for energy transfer.

Some of the kinetic forms which homogeneous catalytic reactions may take are outlined by Hinshelwood (4). He also considers various solvent effects from the same general point of view as homogeneous catalysts. A quantitative kinetic pursuit of such matters in liquid systems involves the necessity of knowing the collision number between solute and solvent molecules.

This problem has been attacked by Jowett (5) and by Moelwyn-Hughes (6). The latter has developed a formula for the calculation of this number which in its development uses the reciprocal relation between viscosity and diffusion coefficient

$$\underline{D} = \underline{RT} / 6 \pi \eta r N$$

His formula makes the collision number proportional to the viscosity and it therefore decreases as the temperature increases. The physical recourse to explain this would be an increase in the free space of liquids. However, experimental work on the viscosities of liquids denies this conclusion (7).

The writer feels that the theory of the structure of liquids advanced by C. V. Raman (8) and supported at the time by W. H. Bragg has much to recommend it. Raman points out that on account of the difference in potential energy of molecules, e.g., in the crystalline state, and when they are free from each other, some of the molecules must be in that state above the melting point. In other words above the melting point we have within the liquid submicroscopic crystals which may, however, differ from macrocrystals in certain ways.

Their presence has been deomonstrated experimentally (9) by G. W. Stewart and others; an extreme case is represented by "liquid crystals". Herzfeld (10), in discussing the viscosities of ideal liquids (11), shows that a "jumping of momentum" effect, i.e., high velocity transmission of momentum through molecules themselves by means of elastic waves becomes a large factor in such liquids. Raman assumes that such high velocity transmission of momentum occurs through his microcrystals so that the viscosity of the liquid would be augmented in proportion to the fraction of the volume occupied by such microcrystals. This fraction is in turn determined by the Boltzman law, and would decrease exponentially with increase in temperature as the viscosity of simple liquids such as benzene does.

This factor tending to augment the viscosity of liquids would hinder diffusion to a corresponding extent and would therefore account for the reciprocal relation existing between these two quantities.

If we are to accept the reasonableness of this picture of the structure of liquids it should be emphasized that what appears to be a homogeneous reaction in solution might turn out to be a heterogeneous reaction occurring on the invisible surface of the microcrystals. The extent to which properties of liquids may be accounted for by this assumed structure of liquids has not been investigated experimentally.

Catalysis by Ions in Solution

The interesting possibility that electrostatic perturbations may be of great importance in chemistry renews our interest and confidence in the large amount of work which has been done on acid and base catalysis, and renders desirable a summary of accomplishments.

J. N. Brönsted (private communication) summarizes his work on acid and basic catalysis in the following statement:

"My ideas on acid and basic catalysis (or protolytic catalysis, as I should like to designate the two effects) is that the catalysis is not only ascribable to the hydrogen (H_3O^+) or hydroxyl (OH^-) ion, (or, for the case of protic solvents other than water, to the corresponding protolytic ions of the solvent) but to all acid and basic molecules at a proportion, that depends upon their strength as acids and bases. For a number of cases there has been shown to exist a linear relation between log k and log K, where k is the catalytic constant of the acid or base and K the strength constant. In this plot, however, statistical factors have to be considered."

Twenty-four references (12) are included.

The work of Dawson has been summarized by Moelwyn-Hughes (13) and need not be repeated here. Suffice it to say that Dawson suggested that in accounting for catalytic reactions in solution, the contributing effect of all species present must be taken into consideration. He has succeeded in evaluating the contributions of the various participating species in certain instances such as the enolization of ketones and the hydrolysis of esters.

Moelwyn-Hughes (14) has also reviewed the work of Lowry on "prototropic" and hydrolytic changes. Lowry appears to regard these processes as being similar to electrolysis. Thus when such changes are catalyzed by acids in aqueous solution, the following steps are involved:

(1) "the reactant molecule collides with a proton-donor, giving rise to an acid complex; (2) this complex collides with a molecule of water; whereby (3) internal electrolysis of the reactant molecule results, the water acting as a proton acceptor in the case of prototropy and as a hydroxyl donor in the case of hydrolysis."

This theory is cited in explanation of the efficiency of amphoteric solvents.

In his general review of catalysis in solution, Moelwyn-Hughes (15) has analyzed some complex cases such as the mutarotation of glucose and finds the effects of some of the participating species such as hydrogen ion are of such magnitude as would be given by

$$\text{Number of molecules reacting / Total number of collisions} = \underline{e}^{-\underline{E}/\underline{RT}},$$

where, in this instance, the total number of collisions refers to those between hydrogen ion and reactant, and $\underline{E}$ is the experimentally determined energy of activation.

Moelwyn-Hughes (16) also makes clear the position of activity coefficients in reactions in solution. He says:

"The study of reactions in solution, including changes undergone by both ionized and un-ionized molecules, affords evidence for regarding the instantaneous rate of reaction (-dc/dt) as directly dependent upon the concentration of reactants. If the reactant molecule is engaged in maintaining a state of equilibrium by combination with either the solvent or any other compound, its concentration becomes indissolubly connected with its activity coefficient, which enters into the kinetic scheme solely on account of this circumstance. Accepting this interpretation as correct, we may look upon parallelisms between velocity coefficients and activity coefficients as evidence that the reaction concerned entails the establishment of such equilibria. When the chemical reaction per se proceeds to completion, the equilibrium must relate to interaction between reactant and solvent."

On page 150 the way in which a velocity constant may be related to activity coefficients is illustrated.

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CHAPTER II

TRENDS IN THE CURRENT APPLICATION OF CATALYSTS

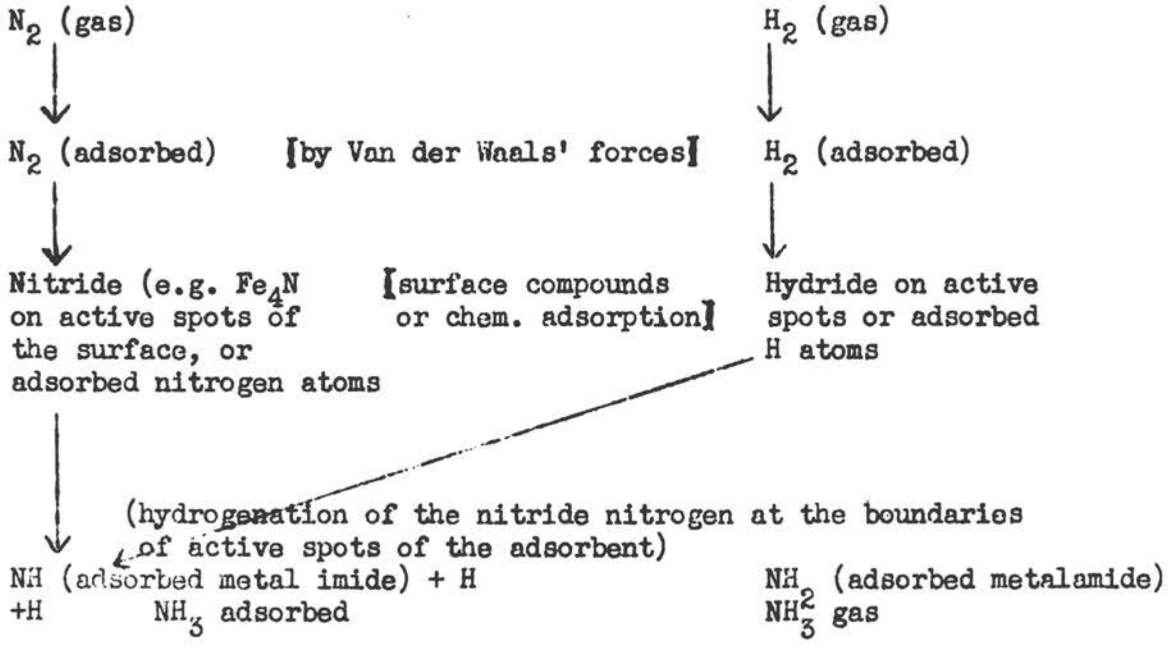
Hydrogenation

(a). Petroleum and Coal. This development which was started by Bergius and is being developed by the Standard Oil Development Company (1) and by the I. G. Farbenindustrie A.G. and Imperial Chemical Industries has for its object (i) the production of motor fuels from substances which hitherto gave poor yields of such fuel. (ii) The improvement of lubricating oils, burning oils, etc. (iii) The production of special products.

The catalysts used are not precisely known but judging from recent patents (2) consist of chromium, molybdenum or tungsten oxides or sulfides or mixtures of these possibly with supports or promoters or both. A manufacturing process involving a catalyst involves likewise the necessity for constant efforts to improve the catalyst. This is particularly pressing in the case of this type of process on account of the large capital investment involved, and substantial progress in this direction appears to have been made. Temperatures of 400 to 550°C and pressure of the order of 200 atmospheres are used. The required purity of hydrogen is not as great as in some other cases of hydrogenation. It contains hydrocarbons and oxides of carbon.

The process at the moment appears to fall a little short of being economic as applied to the problem of making motor fuel (3) in the United States but large plants are in operation for making lubricating oils. The process is a world asset of great value.

(b). <u>Nitrogen</u>. The fixation of nitrogen by causing it to combine with hydrogen has been one of the most romantic applications of catalysis. The technical process has been described by C. Müller (4). The present state of the theory involved has recently been reviewed by Frankenburger (5). The scheme which he supports is:



Some of the implications of this mechanism have been discussed in Chapter I of this report. This reaction, or rather the reverse of it, the thermal decomposition of ammonia has been the subject of many theoretical catalytic studies reference to which may be found in Frankenburger's papers. The writer wishes to emphasize the importance of knowing a great deal about one reaction such as this one as well as something of many.

The catalyst actually used technically in this reaction is thought to be basically iron. It may be supported by alumina and promoted by alkali oxides. The temperature used (in the Haber process) is about 500°C and the pressure about 200 atm. It is also thought (6) that the world is at the moment oversupplied with plants for the synthesis of ammonia.

(c). Oxides of Carbon. The results obtained vary widely depending upon the catalyst employed.

A pure and inexpensive methanol has been made available by the use of catalysts which are believed to be zinc oxide with additions of chromium copper, etc. In any case such catalysts can be used (7). The pressure used is thought to be about 200 atmospheres and the temperature less than 450°C, depending upon the activity of catalyst. This process is a well-established component of the chemical industry. It is thought to coordinate with ammonia synthesis as practiced, e.g., by E. I. du Pont de Nemours and Company.

When dehydrating components are in the catalyst, higher alcohols result at high pressure and dimethyl ether at low pressure (8). Among the higher alcohols are n-propanol; isobutanol; 2 methyl-1-butanol; 2-methyl-1-pentanol; 2, 4-dimethyl-1-pentanol; 4-methyl-1-hexanol; isopropanol; 2-methyl-2-butanol; and 2, 4-dimethyl-3-pentanol (9). It is thought that the ability to produce normal alcohols gives the process an advantage over that involving the addition of sulphuric acid to olefines with subsequent hydrolysis. The process is operated, e.g., by E. I. du Pont de Nemours and Company (10). The mechanism of this formation of higher alcohols has been discussed by Graves (9), and by Frolich and Cryder (11).

Somewhat related to the process of synthesizing higher alcohols from CO and H_2 is that of Fischer and his colleagues (notably Tropsch) for synthesizing liquid fuel from the same starting materials (12). It is stated (13) that on Ni, Co and Fe, higher hydrocarbons are the only product (except water) at temperatures less than 200°C. Pressures used in this process are nominal. This process also appears to be under development in Japan (14). While any process offering the possibility of making motor fuel from CO and H_2 is of military interest to countries like Germany and Japan, this process does not seem to have gained a substantial commercial footing as yet. With prices of crude oil and motor fuel what they have been in the United States, one cannot afford much expense in the production of the latter. The catalysts mentioned do not appear to be robust ones from the point of view of poisoning. The process also appears to involve the scrubbing of relatively small amounts of liquid from large amounts of gas and high recirculation ratios. Methane appears to be a by-product which restrains attempts to increase temperatures. Whether these are the real difficulties involved in process or whether the process is fundamentally inferior to Berginization for motor fuel production, the writer cannot say (15).

Other products may be produced by hydrogenation of oxides of carbon which, however, at the moment appear to be of less importance (16).

(d) Hydrogenation of C = C Double Bonds. The classic example here is of course the hardening of fats as practiced, e.g., by the Procter and Gamble Company. According to J. E. Taylor of that Company (17), the preparation of oil for hydrogenation is well described by Maxted (18). Taylor goes on to say: . . ."the catalysts that have been used most industrially are prepared by reduction of nickel carbonate supported on kieselguhr, mixed nickel and copper carbonates, and nickel formate. The preparation and reduction of the first two are described in Ellis's "Hydrogenation of Organic Substances" paragraphs 1115-1122 and 3722-26. The process of wet reduction of nickel formate and mixed copper and nickel carbonate is discussed in paragraphs 1132-38 and the preparation of the mixed nickel-copper catalyst is described in paragraph 3713. ". . . The process of hydrogenation goes very well in a simple machine like that described by Ellis, paragraph 3710. Hydrogenation is carried out as described in paragraphs 3725 . . . nickel can be recovered by the process described in paragraphs 3721-30."

This is the only process of industrial importance coming under this head which the writer is aware of. It is, however, a reaction which proceeds with extreme ease and many other examples have been investigated (19).

The reverse reaction has recently become of interest in connection with the desire of converting natural and refinery gases to olefines and perhaps to motor fuel (20).

(e) Other Hydrogenations. The hydrogenation of nitrobenzene to aniline is thought to be in commercial operation. Iron is a suitable catalyst (21), though others may be used. The Dow Chemical Company is thought to have a superior process for aniline production in the catalytic reaction of ammonia and chlorbenzene.

Production of Hydrogen

This process, too, in its most economical form has become catalytic. Water gas may be produced by:

$$C + H_2O \overset{1000^\circ C}{=} CO + H_2$$

$$C + 2H_2O = CO_2 + 2H_2$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

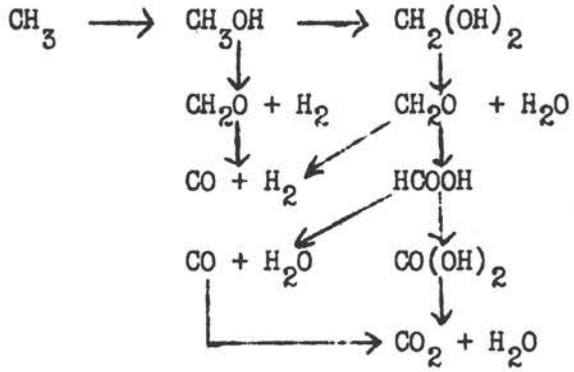
$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

While coal is usually treated with steam at high temperature and in the absence of catalysts consciously added, the treatment of hydrocarbons for the production of hydrogen is strictly a catalytic process. It may be carried out at about 875°C, and nominal pressures. Nickel is thought to be a suitable catalyst (22). Both processes are in large scale operation.

Each is followed by the catalytic step $CO + H_2O \longrightarrow CO_2 + H_2$, which is carried out at 400-500°C and nominal pressure over a catalyst which is thought to be promoted iron oxide. It is evidently highly desirable to lower the temperature at which the first step occurs, which might go so far as to render the second step unnecessary.

Catalytic Oxidation.

On account of the fundamental position which this reaction occupies not only in life processes themselves but in the means we have devised to support life, and to amuse ourselves and make ourselves comfortable, it may not be too much to say that oxidation is the most important type reaction. Whether or not oxidations generally are to be considered as catalytic reactions is an open question depending upon the breadth of our definition of a catalyst and upon the precise mechanism of oxidation reactions. Even the simplest cases are in reality complex as may be illustrated by the reaction, $2H_2 + O_2 \longrightarrow H_2O$ (24). Oxidation reactions are often "chain" reactions. While it has frequently been inferred that this means "thermal" chains, the writer continues to feel (25) that this point of view has been presented entirely too favorably. Definite evidence has been presented in some cases that the chains are "material" in nature in some cases, that is, that they are propagated by rather definite molecular species, however strange the species may appear. In this case, since these propagating and therefore accelerating species are different from the apparent reactants, such cases may be considered as catalytic reactions. Others (26) suggest that the reactions are catalytic in a more usual sense in that peroxides are formed as intermediate compounds which catalyze the oxidation reactions. Still others suggest mechanisms which do not necessarily involve catalysis. Thus Bone (27) appears to believe that oxidation of hydrocarbons proceeds by a mechanism illustrated by



It is thought that the kinetic method has not been sufficiently employed in arriving at this conclusion.

A recent description (28) of the high pressure oxidation of the lower paraffins shows that the major product in each case is alcohols. The Bone mechanism does not necessarily deny a participation of catalysts.

Yet another school of thought (29) would have preliminary dehydrogenation play an important part in oxidation processes. Catalytic agents could readily play a part here.

Whether or not all oxidation reactions are inherently catalytic, it is well enough established that they are very subject to catalytic action.

The primary application of oxidation is in combustion for heating and power generation. Here the natural propensity of the reacting system to rise in temperature with corresponding increase in speed largely obviates the necessity for introducing catalysts. Nevertheless, a certain amount of combustion space must be allowed in furnaces in order to allow the reaction adequate time to complete itself which might to advantage be cut down (30). Bone in his surface combustion has shown how catalysis may be applied usefully for combustion. The principle is in common practice in household heating with gas and a specialized combustion catalysis is exemplified by the waning Welsbach mantel.

While with complete combustion the products are simple even though the mechanism may be complex, in the case of partial combustion both the products and the mechanism are ordinarily of great complexity which tends to limit the usefulness of this application. Starting with aliphatic hydrocarbons, not only may one get a wide variety of oxygenated compounds (31) but depending upon the conditions the products of decomposition of the hydrocarbons may also be obtained (32).

In this connection, however, F. Fischer and H. Pichler (33) have suggested the synthesis of acetylene from methane and other hydrocarbon gases by means of dehydrogenation with oxygen.

The complexity of homogeneous (uncatalyzed?) oxidation reactions renders the application of selective catalysis important if these reactions are to be simplified for synthetic purposes. While oxidation products of some complexity are now made commercially (34), that produced on the largest scale being in all probability "blown" asphalt of the petroleum industry, the widest successes in oxidation synthesis have been in just those cases where a high degree of simplification has been achieved through the application of selective catalysis.

This is well illustrated by the oxidation of naphthalene to phthalic anhydride, as practiced, e.g., by the Monsanto Chemical Company. The fundamentals of this process were worked out by Gibbs and Conover (35). Catalysts consisting of oxides of molybdenum, vanadium, etc. are thought to be suitable, at 350 to 550°C and at nominal pressures. The phthalic anhydride may be broken down to benzoic acid catalytically, a practical process being used by the Monsanto Chemical Company (36).

An adaptation of the process is also practical for the oxidation of anthracene to anthraquinone (37).

When the starting material is benzene in a similar process, maleic anhydride is the principal product (38). This process is thought to be in operation by the Barrett Company but is of less importance at the moment than the oxidation of naphthalene and anthracene.

While it seems to be easier to achieve catalytic simplification and selection of oxidation reactions with aromatic starting materials than with aliphatic, processes are being suggested for the oxidation of aliphatic hydrocarbons. For example (39) very substantial yields of methyl, ethyl and propyl alcohols appear to be possible in the oxidation of propane at 136 atmospheres and 300-350°C. Difficulties appear to be (a) small possible conversion per pass, (b) introduction of oxygen and (c) separation of products (40).

Another example of the production of relative pure chemical substances by the oxidation of aliphatic hydrocarbons is that sponsored, e.g., by the I.G. Farbenindustrie for making acids suitable for soap manufacture by the oxidation of paraffin wax (41).

Other practical processes involving catalytic oxidation consist of the oxidation of alcohols to aldehydes with catalysts such as copper and silver (42). The precise economic position of these processes is, however, not known to the writer.

In the field of inorganic catalytic oxidations, the oxidation of sulphur dioxide in manufacture of sulphuric acid in which platinum, oxides of nitrogen, and vanadium pentoxide are employed as catalysts, and the oxidation of ammonia in the manufacture of nitric acid in which platinum and base metal catalyst consisting of iron oxide with possible addition of bismuth, copper, etc. may be used as catalysts, are outstanding (43).

The removal of H_2S from gas by means of hydrated ferric oxide may be catalytic when oxygen is present, although as often practiced is an intermittent one, not truly catalytic.

Polymerization and Condensation Reactions

The growth of the synthetic plastic industry, the start which has been made in commercial synthetic rubber manufacture in the United States (44), commercial production of special lubricating oils by the polymerization of high molecular weight olefines (45), the opportunity offered by the huge quantity of olefines produced by cracking petroleum fractions or which would be available by cracking such fractions for the application of polymerization reactions (46), and various other factors have stimulated a growing interest in polymerization and condensation reactions.

The field of synthetic rubber has been rather elaborately reviewed by Whitby and Katz (47).

Carothers and his colleagues (48) have been studying reactions such as the esterification of dibasic acids with glycols, the action of sodium on di bromides, etc. in connection with a general study of polymerization.

Studies of polymerization reactions where high molecular weight compounds result become involved in complexities due not only to the complex structure of a single molecule but to the fact that a single molecule is not and cannot very well be formed as a product. While most studies in this field are from the organic or industrial point of view, it is evident that a study of mechanism by the kinetic method would also be embarrassed by complexity due to the variety of courses which the reaction may take. Such studies are nevertheless to be recommended.

H. Staudinger's "Die Hochmolekularen Organischen Verbindungen", (Julius Springer, Berlin, 1932) is a recent contribution (500 pages) to the field. Our ignorance of mechanism in this field is accompanied by an ignorance substantially as deep of the viscosity of liquids. Staudinger (49) concluded that many of the high molecular weight compounds have linear structures and that their viscosities are to be accounted for on the assumption that these molecules spin and thus occupy a volume which Einstein's formula (50) (and the measured viscosity) would suggest. The objection to this picture is that the density of, e.g., styrene to which Staudinger's theory was particularly applied goes up as polymerization proceeds (51). Einstein's point of view may also be correlated with that of Raman on the structure of liquids which has been outlined in the theoretical section of this report (page 132).

In order to gain an insight into the mechanisms of the complicated cases, the study of the first steps of simple cases is to be recommended. However, results obtained so far have not given rise to general agreement. Thus it has been proposed that in the polymerization of ethylene (52) the first step may be:

$$2C_2H_4 \longrightarrow C_4H_8 \text{(butylene)}$$

$$3C_2H_4 \longrightarrow 2C_3H_6 \text{(propylene)}$$

$$2C_2H_4 \longrightarrow C_4H_6 \text{ (butadiene)} + H_2$$

$$C_2H_4 \longrightarrow \underset{\substack{\downarrow \\ \text{polymerization}}}{C_2H_2} \text{ (acetylene)} + H_2$$

Polymerization reactions are very subject to catalytic action. It has been suspected that the presence of oxygen has a marked effect on them (53). This suspicion has been confirmed by Conant and Tongberg, by Conant and Peterson (54) and by Adkins and Houtz (55) for the polymerization of styrene.

The writer and H. E. Thompson (56) have found that citral purified by distillation in high vacuum and preserved in a "corex" tube, contrary to its usual behavior, underwent no apparent change in three years, and would withstand exposure of many hours duration in direct sunlight or the full radiation of a mercury vapor lamp without polymerization.

The part played by oxygen in the formation of gum in cracked gasoline is well known.

The writer therefore wishes to suggest that before attempts to correlate molecular structure with propensity to polymerize are carried too far, that the part played by catalysts in these processes be given adequate consideration.

The best known application of the interrelation of oxidation and polymerization is in paint driers where positive oxidation catalysts are used to achieve a result which could be arrived at (and perhaps with better results) by polymerization alone. These catalysts consist of lead, manganese, cobalt, aluminum, calcium, zinc, and cadmium soaps (58).

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RESTRAINT OF SLOW OXIDATION REACTIONS

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Cracking coil distillate which constitutes approximately 50% of our present motor fuel, deteriorates on storage. This deterioration is accompanied by a loss of knock rating and the formation of gum. Both of these results are highly undesirable in that they seriously interfere with the performance of the fuel in the automobile motor. For example, losses of knock rating in the neighborhood of 20% have been reported from six months storage of a cracked gasoline (1).

The amount of gum formed may also be very considerable and may even amount to several hundred milligrams per 100 cc. of gasoline, from a few months of storage. This gum may deposit in the induction system of a motor so as to interfere with or even prevent engine operation. The deterioration of cracking coil distillate has been shown to result from a process of oxidation of the unsaturated hydrocarbons present, accompanied by polymerization (2). The oxygen absorption curve (the conventional oxygen bomb stability test) of the cracked distillate with time shows a measurable induction period. The rate of oxygen absorption is markedly susceptible to catalytic influence. Pro-oxidants notably copper (the conventional copper dish test for gum stability) and copper salts reduce this induction period, and antioxidants (inhibitors) serve to lengthen it. In the class of antioxidants, phenols and their derivatives (1, 3) are especially effective.

Egloff and coworkers (4) have correlated the effectiveness of an inhibitor with its critical oxidation potential, the effectiveness being measured by the induction period in the accelerated oxidation test.

The same type of chemical compounds have been successfully applied to the analogous case of inhibition of deterioration of rubber by oxidation on ageing (6).

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ANTIKNOCK COMPOUNDS

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Another very important example of the practical utilization of oxidation inhibitors is furnished by the use of antiknock agents to prevent knocking in internal combustion engines. The efficiency of the Otto cycle engine increases with a decrease in the volume to which the charge is compressed before firing. Unfortunately, the corresponding increase in pressure and in temperature causes the occurrence of an extremely rapid and violent combustion of that portion of the charge which is the last to burn. This phenomenon is readily noticeable by the clicking metallic noise which it causes and from which it derives its name of "knock". The knock causes loss of power, overheating and excessive wear of engine parts, thus making it imperative to keep the compression below a safe limit.

Although the combustion processes which result in knocking are by no means clearly understood, it is evident from recent investigations (1) that the phenomenon is dependent in general on the chemical nature of the fuel and in particular on the occurrence of slow oxidation reactions in the air-fuel mixture prior to its inflammation. The tendency to knock is suppressed by retarding or preventing this slow oxidation, and one of the simplest methods of accomplishing this is by the use of antiknock agents which function, at least in part, as oxidation inhibitors.

The quantitative measurement of knock itself has been the subject of a considerable number of investigations in recent years. The outstanding result of this search, as far as the present review is concerned, is the recognition that its occurrence and intensity vary greatly with every variable which may affect the operation of an internal combustion engine. Suffice it to name a few of the most significant variables: nature of the fuel, operating temperature, air-fuel ratio, compression ratio, speed. Not only does each variable affect the tendency to knock, but each change in conditions usually has a different effect on different fuels. To illustrate: a gasoline-benzene blend gives the same performance under a given set of conditions as a lead-treated fuel; the cooling jacket temperature is raised, and the benzene blend knocks much more than the leaded fuel. Again: A blend of straight run and cracked MidContinent gasoline is prepared which matches a California gasoline; the same small amount of tetraethyllead is added to both, and the California fuel becomes far superior to the Mid-Continent gasoline. Likewise, the relative value of various fuels and the relative effectiveness of various antiknock agents will change with the conditions of the test. A study of these variations would be outside of the scope of the present paper.

For these reasons the overall relative effectiveness of various compounds as antiknock agents cannot be reported with any great degree of accuracy unless the exact conditions of testing are fully specified. Since data reported by different laboratories were usually obtained under different conditions, the figures given below may vary from other data reported elsewhere on the same compounds. It will, however, be fair to assume that these figures correspond reasonably well to operation in a standard type of automotive engine.

A list of some typical antiknock compounds is given in Table I.

TABLE I

Relative Effectiveness of Antiknock Compounds (5).

Reciprocal of number of moles giving the same antiknock effect as one mole of aniline.	
Benzene*	0.085
2,2,4-Trimethylpentane*	0.085
Ethyl alcohol*	0.104
Xylene*	0.142
Aniline	1.000
Ethyl iodide	1.09
Titanium tetrachloride	3.2
Diethyl selenide	6.9
Diethyl telluride	26.6
Nickel carbonyl	35.
Iron carbonyl	50. (approx.)
Tetraethyllead	118.

* These compounds are commonly regarded as non-knocking fuels rather than as antiknock agents. They are included here for the purpose of comparison.

As will be seen from Table I, antiknock agents, in general, fall into three categories: (a) inert fuels; (b) organic inhibitors and (c) metallic compounds.

The first class comprises relatively stable hydrocarbons such as benzene and 2,2,4-trimethylpentane ("isooctane"). Comparatively large percentages of these hydrocarbons must be used before any noticeable effect is observed on the tendency to knock. For this reason, they are usually considered as non-knocking fuels rather than as antiknock compounds, and their effect is attributed to dilution of the knocking fuel. In the absence of an absolute scale of measurement of antiknock action, it is impossible to determine by an engine test whether the effect obtained is merely the sum of the partial effects of the two fuels or whether the non-knocking fuel also acts as an inhibitor of the knock caused by the other fuel with which it is mixed. There is at least a suggestion that the latter is correct: Mardles (6) has shown that benzene inhibits the slow oxidation of _n_-hexane and cyclohexane, and Beatty and Edgar (7) have found a similar effect of 2,2,4-trimethylpentane on the rate of oxidation of _n_-heptane.

The second class comprises the organic compounds of nitrogen. Table II gives the relative effectiveness of a comprehensive group of compounds of this class.

TABLE II

_A_. Influence of Some Groups Attached to the Atom on the Antiknock Effect of Nitrogen (8)
Reciprocal of number of mols giving the same antiknock effect as one mole of aniline.

Ammonia	-0.09 (proknock effect)
Ethylamine	0.20
Diethylamine	0.495
Triethylamine	0.14
Diethylaniline	0.24
Ethyldiphenylamine	0.58
Triphenylamine	0.09

(Table II. A continued)

Diphenylamine	1.5
Phenylamine (aniline)	1.0

B. Effect on the Antiknock Value of Aniline of Substituting Various Organic Radicals for Hydrogen in the Ring and in the Amine Group (8)

Aniline	1.0
Toluidine	1.22
m-Xylidine	1.4
Cumidine	1.51
Ethylaminobenzene	1.14
n-Propylaminobenzene	1.10
n-Butylaminobenzene	1.11
Amylaminobenzene	1.15
Aminobiphenyl	1.14
Monomethylaniline	1.4
Monoethylaniline	1.02
Mono-n-propylaniline	0.75
Mono-n-butylaniline	0.52
Mono-isoamylaniline	0.248
Diphenylamine	1.5
Dimethylaniline	0.21
Diethylaniline	0.24
Di-n-propylaniline	0.27

As a class, the nitrogen compounds are far superior to the non-knocking hydrocarbons. Indeed, many of them are better than aniline, which is about 12 times as effective as benzene, one of the best hydrocarbons. It is quite clear, moreover, that the effective antiknock agent is not the element nitrogen (nitro compounds are knock inducers) but rather a special type of linkage between it and organic radicals. Thus, the least effective compounds are those containing no aromatic linkage to the nitrogen, while the most effective contain at least one such linkage and at least one N-H linkage. This is probably linked with some oxidation or oxidation-reduction process to which compounds of this type are particularly susceptible.

The third class comprises compounds of metallic or non-metallic elements, in which the antiknock action is identified more closely with the element itself, and is less affected by the type of compound in which the element is present.

This class of compounds covers a wider range of effectiveness than the nitrogen compounds; it also comprises the most effective antiknock compounds known. Tables III and IV give the relative antiknock value of several compounds of the same elements.

TABLE III

Relative Antiknock Effect of Ethyl and Phenyl Compounds of Four Elements (9).

Reciprocal of number of moles giving the same antiknock effect as one mole of aniline.

Element	Ethyl Compound	Phenyl Compound
Iodine	1.09	0.88
Selenium	6.9	5.2
Tellurium	26.8	22.0
Oxygen	-0.036 (proknock effect)	0.122

TABLE IV

Relative Antiknock Effect of Various Organo-Lead Compounds (10)

Reciprocal of number of moles giving the same antiknock effect as one mole of tetraethyllead.

Dibutyldiphenyllead	0.33
Diisobutyldiphenyllead	0.38
Di-sec.-butyldiphenyllead	0.45
Tetraethyllead	1.00

Our knowledge of the mechanism of antiknock action is still very scant. The main reason for this is probably that we still know very little about the mechanism of the simple combustion of hydrocarbons. A few facts, however, appear to be rather generally accepted at present:

1.- The preliminary stages of the oxidation of hydrocarbons comprise the formation of reactive oxygenated products (2,3).

2.- A certain amount of oxidation takes place in the unburned portion of the fuel charge in an internal combustion engine (4,11) under conditions of incipient knock.

3.- This amount of oxidation increases with the intensity of the knock (4).

4.- The addition of an antiknock agent appears to decrease this amount of precombustion oxidation (2).

5.- When knock occurs, combustion spreads at a high rate of speed throughout the unburned mass, or may even start spontaneously and very rapidly throughout this mass (4,12).

Based on the above facts, and by analogy with the suggested mechanism for the action of oxidation inhibitors, the following mechanism has been suggested for antiknock action:

(a) The unburned fuel ahead of the flame front is being heated by radiation and by adiabatic compression. It undergoes partial oxidation with the formation of oxygenated products whose chemical activity is sufficient to initiate chain reactions of oxidation. When the chain reaction velocity reaches a critical value, the whole mass of unburnt fuel reacts explosively, and the sudden increase in pressure causes the phenomenon known as knocking.

(b) Antiknock agents act as deactivators or inhibitors of these chain reactions. This mechanism of the inhibition of a chain reaction satisfactorily explains the extreme effectiveness of some antiknock compounds, such as tetraethyllead, one molecule of which exerts a noticeable effect on the combustion of 215,000 molecules of a kerosene-air mixture.

No light has been thrown as yet on the actual mechanism whereby this inhibition is achieved. None of the compounds involved are stable under the conditions existing during combustion. It is safe to assume, therefore, that at least the organic antiknock compounds exert their action mostly on the oxidation which takes place in the unburned mass ahead of the flame front. To what extent they themselves undergo oxidation in the process of deactivating the oxygen carriers has not yet been ascertained.

The metallic antiknock compounds may likewise act before ignition. They will, however, yield by oxidation compounds which are stable in the flame, and which, therefore, may still be active during the process of ignition. Pidgeon and Egerton (13) have already shown that tetraethyl lead must be oxidized before it becomes effective in reducing the rate of reaction of a mixture of pentane and oxygen in a glass vessel under 400 mm.

total pressure and at 265°. It would appear therefore, that at least some of the effect of this type of inhibitor is directly attributable to the oxide of the metal. On the other hand, organo-metallic compounds are also effective as oxidation inhibitors in the liquid phase at room temperature, under conditions under which they are normally quite stable (14). It is conceivable, therefore, that they are effective both before and after ignition, and that their great effectiveness is due to a reversible process of deactivating the oxygen carriers, involving an equilibrium between two degrees of oxidation of the metal.

A large amount of work has been done on the effect of antiknock agents on the ignition temperatures and on the oxidation of hydrocarbons. This in general confirms the relationship between these processes, while at the same time revealing marked differences between them. For this reason, the best way to gain more insight into the mechanism of knock and its suppression probably lies in the direction of a study of combustion in the engine, before and after ignition, by chemical analysis, a study of the emission and absorption spectra, etc.

The commercial value of antiknock agents is a complex function of their effectiveness, cost, and some of their other properties, such as stability, freedom from harmful effects on human beings or engines, etc. Although the field has been scanned carefully by many investigators, as evidenced by the patent literature, over the 13 years since Midgley and Boyd disclosed the results of their fundamental work, only tetraethyllead, iron carbonyl and aniline have ever received any serious consideration as commercial antiknock compounds.

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SYNTHETIC PLASTICS

Some of the synthetic plastics which are manufactured or have been suggested for manufacture are representatives of condensation reactions, while others are polymerizations.

Scheiber and Sändig (1) list the technically important resins as the following:

(1) Cumaron resins. These are produced by the polymerization of certain fractions of solvent naphtha under the influence of sulphuric acid.

(2) Aldehyde resins. These are produced from acetaldehyde, crotonaldehyde and the like by action of condensing agents such as alkalis and sulphuric acid.

(3) Phenol-aldehyde resins. These are made from phenols and aldehydes by using a variety of condensing agents such as acids. By varying the structure of the phenol and the aldehyde and by varying the condensing agent products with various properties may be obtained.

(4) Urea-formaldehyde resins. The condensation between the urea and the formaldehyde may be carried out without condensing agent or with acids or basic condensing agents. The nature of the product, of course, varies according to the process chosen.

Resins of the "glyptol" type are also thought to be of importance. These are reaction products of phthalic anhydride and polyhydric alcohols.

The Goodyear Tire and Rubber Company appears to be entering this field with a synthetic molding resin made by the action of chlorostannic or chlorostannous acid on rubber. This paper indicates some relations between the rubber field and the resin field. A further development in this field by

Thomas and Carmody is discussed later.

It is evident that the wide variety of starting materials, catalysts, and conditions which may be employed to obtain resinous products of various kinds outline the course of a vast amount of experimental work.

Hydration and Dehydration

The application of catalysis to hydration and dehydration reactions is very important in the laboratory and has likewise achieved various successes in industry.

Thus, as is well known, ether is made from ethyl alcohol by catalytic dehydration using sulphuric acid, phosphoric acid, etc., as catalyst.

Hydrolysis of fats may be placed in this classification. A. S. Richardson (private communication) recommends Lewkowitsch's discussion of the Twitchell process (6). Twitchell's reagent or any high molecular weight sulfonic acid may be used. The autoclave process is also discussed by Lewkowitsch (6). The catalyst used here is a soap, particularly calcium or zinc soap.

The direct hydration of olefines to form alcohols is an attractive paper reaction in view of the vast quantities of olefines available from cracked gases. Experimentally, however, the tendency of the olefines to polymerize appears to be a very disturbing factor. The hydration via sulphuric acid (7) is, however, in commercial practice for making ethyl and isopropyl alcohols.

The hydration of acetylene to acetaldehyde is thought to be commercially established. Mercury salts and other compounds may be used as catalysts (8).

Catalysis has long been used in the manufacture of esters, which have found wide application as solvents, especially in lacquer manufacture. Not only do we have the usual reaction of an alcohol with an organic acid which may be catalyzed by mineral acids, but it has been proposed to form esters by the direct catalytic reaction of an olefine with an acid (9), and also by the reaction of aldehydes with themselves under the catalytic influence of aluminum alcoholate (10).

The elimination of water between an alcohol and ammonia or an amine is thought to be a practical procedure for the manufacture of amines (11). The standard types of dehydrating catalysts are thought to be effective.

Halogenation

The outstanding example under this heading is the chlorination of benzene, catalyzed by iron (12). "Carriers" for the other halogens are listed by Maxted.

The addition of hydrochloric acid to olefines is catalyzed by halides of antimony and bismuth (13). This may be an important process in view of the large uses for ethyl chloride which have developed.

Antimony fluoride has been applied in the technical fluorination of organic compounds (14).

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The Application of Aluminum Chloride as a Catalyst

H. P. Lankelma

Since the publication in 1877 by Friedel and Crafts of a new method of synthesising hydrocarbons, ketones, etc., which involved the use of anhydrous aluminum chloride as the catalytic agent, an enormous amount of work has been done utilizing this material in synthetic work. In general aluminum chloride has been used to bring about the linking of carbon to carbon through reactions involving exchange or addition, molecular rearrangements including changes in carbon skeletons, the addition of certain reagents to olefines, and dehydrogenation.

In spite of the fact that numerous investigators have studied the problem, no general satisfactory interpretation of the action of the aluminum chloride in catalyzing these reactions has been reported.

Friedel and Crafts (1) in the synthesis of benzoic acid from benzene, carbon dioxide and aluminum chloride suggested an intermediate product $C_6H_5Al_2Cl_5$. That intermediate compounds between the reactants and aluminum chloride are formed has been shown by a number of workers and a large number of such compounds have been isolated and reported (2).

Steele studied the reaction velocity in the formation of tolyl phenyl ketone from toluene and benzoyl chloride in the presence of aluminum chloride(3) and obtained evidence to show that the aluminum chloride forms addition products with both of the reactants, depending upon the ratio of aluminum chloride to acid chloride employed. However, the role of these intermediate compounds in the main course of the reaction is not well understood. The well known (4) deviations of the effect of variation of concentration of aluminum chloride from the ordinary effects of variation of the concentration of a cateylst, Steel attributes to the fact that this reagent can combine with certain products of the reaction to remove it from the system.

Technical Applications

The development of a technical process for the preparation of aluminum chloride from bauxite (5) has made this reagent available for a number of commercial processes. In the field of organic chemistry, it is employed in the preparation of intermediates and finished products such as dyes, perfume materials and resins and for cracking and purifying petroleum products and polymerizing olefines to lubricating oil.

Dyes and Dye Intermediates

Aluminum chloride is employed to couple cyanuric chloride with α naphthols to form 1,3,5 triazones (6). Oxythionaphthenes are obtained by the action of aluminum chloride upon aryltheoglycollic acid chlorides (7). o-benzoyl benzoic acids are obtained from phthalic anhydride and aromatic hydrocarbons, dibenzopyrenequinones from benzoylchloride and benzanthrone (8), and carbozole derivatives from α α dianthrimidenes (9).

Perfume Materials

Acetophenone is prepared by the action of acetyl chloride on benzene and tert. butyl xylene from isobutylene and m-xylene.

Resins and Resin Intermediates

Ethyl benzene is obtained from ethyl chloride or ethylene and benzene.

A new synthetic resin having various industrial possibilities has been produced by the action of aluminum chloride upon suitable cracked petroleum distillates (10).

Lubricating Oil

A lubricating oil of high viscosity index and high oxidation stability is obtained by polymerizing suitable cracked petroleum distillates with aluminum chloride (11). A product for reducing the pour point of lubricating oils without otherwise changing their properties is prepared by condensing chlorinated long chain aliphatic hydrocarbons with a high molecular weight cyclic nucleus in the presence of aluminum chloride (12).

Cracking of Petroleum

Aluminum chloride has been employed in the cracking of petroleum hydrocarbons at lower temperatures than would be required for simple thermal decomposition (13), although the process appears to be scarcely economic at the moment. The hydrogen liberated in the cracking hydrogenates the resulting fragments so that the gases and liquid distillate are largely saturated in character (14).

General

Catalysis has been or may be applied to various technical or potentially technical reactions not considered in detail in the foregoing. Some of these are: the various applications of fermentation, such as the manufacture of ethyl alcohol and butyl alcohol; the entire field of enzyme, vitamine, and hormone action; rubber accelerators; sulphonation of aromatic hydrocarbons; molecular rearrangements; the Gatterman-Kock reaction; the Sandmeyer reaction, etc. They have not been considered more elaborately because of insufficient technical importance or because of the writer's ignorance and lack of contact with the field.

However, within these limitations the applications of catalysis which have been treated are thought to include the major cases from the point of view of present practice and near term prospects. The work is not intended as an adequate, comprehensive treatise, but rather to give an impression which is up to date and tolerably well balanced.

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CHAPTER III

COORDINATION OF THEORY AND PRACTICE

An efficient coordination between theory and practice in the field of catalysis certainly does not exist. Most companies have more pressing obligations than that of educating the world, and this is one reason why it is difficult for anyone else to bring about that coordination. But in addition many theoretical men are restrained on account of training, temperament, or circumstance from undertaking it. It was felt that one procedure might be for companies interested in catalysis to suggest theoretical problems, the solution of which would be of direct value in the application of catalysis.

Dr. E. K. Bolton of E. I. Du Pont de Nemours and Company has, for this purpose, selected the following problems:

(1) The equilibrium of hydrogen, carbon monoxide, and methanol has not been studied under conditions which avoid side reactions. A more accurate study of this equilibrium with side reactions minimized would assist in the interpretation of the behavior of the catalyst.

(2) Methanol may be dehydrated catalytically at high pressure to yield higher alcohols, and at low pressure to yield dimethyl ether. The mechanisms of these dehydrating reactions, their relationship to each other and to the catalyst, are not understood.

(3) The equilibrium of the system carbon monoxide, water, and formic acid has not been studied with precision. Data on this reaction are needed for the better understanding of the mechanism of the catalytic action involved.

(4) A knowledge of the behavior of gases under high pressure is necessary before thermodynamic calculations can be applied with even moderate precision to high pressure catalytic reactions. Carbon dioxide and water are produced in some of these high pressure reactions. The influence of these two substances together on the pressure of the system is not known. A phase rule study of this two-component system at pressures up to 1000 atmospheres would be of value.

Likewise, data are needed regarding the compressibility of binary gas mixtures when one component is relatively easily condensible. A mixture of nitrogen and methanol vapor, nitrogen and ammonia, or carbon dioxide and carbon monoxide are representative examples. A study of such systems at 100°C and at pressures in the vicinity of 1000 atms. would enable one to know whether Dalton's law of partial pressures is valid under these conditions. One method of conducting experiments of this character would be to add a measured quantity of methanol, for example, to nitrogen at high pressure, observe the increase in pressure and compare the final pressure with the value calculated from the application of Dalton's law.

(5) The solubility of hydrogen in pure organic compounds at various temperatures up to 300°C and pressures up to 500 or 1000 atms. would be of value in the study of catalytic hydrogenations. Such data would allow one to study the activity of the catalyst apart from apparent activity caused by an increased solubility of hydrogen with increase in pressure.

(6) The Friedel-Crafts reaction between carbon monoxide and hydrocarbons is worthy of further study.

(7) Active hydrogen has been reported to be ejected from a catalyst

when the hydrogen contains a small quantity of oxygen. There is a possibility that in these experiments the active hydrogen arose from a reaction of the hydrogen with the oxygen in the gas phase. The experiments should be repeated under conditions which would avoid possible activation of the hydrogen by any homogeneous reaction.

A search for free radicals in a beam of reactant molecules reflected from a catalytic surface should be made. After data have been collected for numerous species of molecules and catalysts at various temperatures, important conclusions could probably be drawn regarding the mechanism of many catalytic processes. If the thermal accommodation coefficient were studied at the same time the data would have additional value. A close relationship may exist between catalytic activity and thermal accommodation coefficients. The thermal effects which occur when a molecular beam containing a mixture of molecules capable of reacting at the surface of the catalyst is reflected from this surface may prove very interesting.

(8) Many catalytic theories can probably be given a crucial test by using heavy hydrogen as a tracer of the hypothetical mechanism. For example, the controversial point as to whether palladium and other hydrogenation catalysts form intermediate compounds of some sort with hydrogen could be determined by making an isotope exchange reaction test. A physical mixture of heavy and light hydrogen molecules might be passed through a palladium membrane, and the emergent gas inspected for hybrid molecules. If no hybrid molecules were found, then the gas passed through as though palladium were merely physically porous to hydrogen. However, if hybrid isotopic molecules were formed during the passage, a chemical combination of some

sort with the palladium was involved. Similar experiments with other hydrogenation catalysts, using adsorption — desorption instead of diffusion, would yield valuable information about these catalytic materials. Care would have to be taken, of course, to avoid the occurrence of other possible isotope exchange reactions.

Quantum mechanics predicts that the lighter isotope will be found in general to be more active chemically than the heavier isotope. Measurements of the relative rates of catalytic hydrogenations, using the two species of hydrogen with various catalysts and reactants, would have fundamental value.

(9) The selective halogenation of carbon atoms should be possible if Norris' statement is correct that each carbon - carbon bond in an organic molecule possesses a definite energy level depending upon the environment. No experiments appear to have been done in this direction.

(10) One handicap to the study of many catalytic organic reactions is the lack of accurate analytical methods for examining the products of these reactions. Accurate information about physical properties of pure compounds is needed for the development of appropriate analytical methods. Melting points, vapor pressure curves, density - temperature, and refractive index - temperature curves for pure aliphatic compounds such as the alcohols, aldehydes, ethers, ketones, etc. containing more than five carbon atoms are the data desired.

P-T-X data for binary and ternary mixtures containing four to nine carbon atom aliphatic liquids are needed, for example, the P-T-X data for the system methyl and butyl alcohols and water. There is a possibility that data for one such system might be employed to predict P-T-X data for another closely related system.

The above data would greatly assist the development of practical methods for the determination of:

(a) Primary alcohols in the presence of secondary alcohols.

(b) Aldehydes in the presence of ketones.

(c) Saturated hydrocarbons in the presence of aldehydes.

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Dr. L. V. Redman of Bakelite Corporation suggests the following:

"If and when certain types of organic bodies, such as Bakelite, are polymerized and aggregated together into larger molecular masses by means of catalytic agencies, there is always produced in the material violent changes in its cohesion or adhesion or adsorption to a coated surface; and this change in film construction is sometimes very confusing to us, either because the polymerized material will not adhere to the surface or it adheres too strongly."

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In the field of petroleum chemistry, while important applications of catalysis such as anti-knocks, inhibitors, and hydrogenation have been made, those who aspire to lengthening this list are beset with the following universal restraints.

(a) Variability of raw material due to variation of crude and of refining practice.

(b) The presence of sulfur which poisons many catalysts.

(c) Uneconomic formation of coke in many attempted applications.

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May 3, 1934.