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CATALYSIS

CATALYSIS

From the Standpoint of Chemical Kinetics

BY

GEORG-MARIA SCHWAB

Professor-Extraordinary of Chemistry at the University of Munich

Translated

FROM THE FIRST GERMAN EDITION

with additions from the recent literature by the author,

BY

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AND

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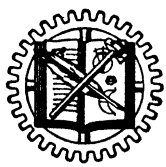

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The records grow
unceasingly, and each new grain of truth
is packed, like radium, with whole worlds of light.

ALFRED NOYES — *The Torch-Bearers.*

TRANSLATOR'S PREFACE

THE first German edition of Dr. Schwab's book obtained such a favorable reception in English-speaking countries that permission was at once sought and obtained to make an English translation of the book. It was felt that the material presented formed an excellent basis for courses dealing with the fundamental principles of catalysis, both in homogeneous and heterogeneous systems. The work of translation was to be shared between Dr. R. Spence and the writer. Before this work was completed the difficult economic conditions in the world had extended to the field of scientific literature. Publication was postponed.

Developments in the field of catalytic reactions by no means suffered to the same extent as conditions in the economic world. When the time came to issue the volume in English it was found necessary to supplement the original text by copious additions from the recent literature. These were supplied both by the author and the translators. How great these additions are can readily be seen in the body of the text since all the additional references have been assigned numbers with letter subscripts. They have permitted a presentation of the subject which, it is hoped, is fairly representative of the present status of catalysis in its broadest aspects. Other volumes have appeared which cover in much greater detail various sections of the present book. No such detailed treatment is possible in a volume of this size. It is hoped, however, that herein may be found a broad and adequate presentation of the subject, such as a young student of the science might be expected to acquire in the course of his graduate work. My thanks are due to the author, who has unreservedly assisted in the improvement of the text, to Dr. Spence for his translation of one-half of the text and to my brother, Professor H. Austin Taylor, who, in my absence from America, has shouldered the responsibility of reading final proofs and providing the indexes.

HUGH S. TAYLOR

LOUVAIN, *July*, 1937

PREFACE

THE significance of catalysis in the field of chemistry is being brought more and more to our attention, encouraged by the development of technology on the one hand and of scientific biology on the other. The perfection of the indispensable physicochemical foundations of catalysis has, in general, kept pace with the consequent increasing necessity for a scientific treatment of the subject, and chemical kinetics particularly, in its present state of rapidly advancing development, affords a generously proportioned substructure. It is true that new, as yet unsolved, and more deeply penetrating problems are now emerging in growing numbers from behind older questions which have been cleared up, but it is precisely for this reason that an attempt at a comprehensive consideration of catalysis from the standpoint of chemical kinetics promises some reward.

To give a somewhat extensive or very exhaustive collection of facts in a very highly compressed form, would correspond neither with the time and space at our disposal, nor yet with necessity. Likewise, explanatory experiments and theories, both new and old, dealing with catalytic phenomena, are only dealt with briefly. The plan followed has been rather, to work out the laws which hold for catalysis generally as well as for its different varieties, and to elucidate and confirm from them the principles by which the influence of catalysts on velocity is possible and by which it occurs. Naturally, our knowledge regarding these questions is often inconclusive, and it so happens that in many places pre-eminence is given, not to the data already at our disposal, but to open problems of research, whose present position is fully discussed. When, in this connection, some of the most recent theoretical propositions are mentioned by way of suggestion, it must also be pointed out that complete agreement with experiment has not as yet been attained.

A treatment of the general basis of catalysis should bear the closest connection with experiment. Major importance has, therefore, been placed on those observations fundamental to the discussion. In the selection of experimental data, regard has been paid to their usefulness in the clarification of questions of principle arising in the individual sections, and of course, no opinion is voiced regarding the large mass of material not taken

into consideration. Not to encumber the account with too many details, references to the original literature have been compiled in a detailed index.[1]

Formulae have been used only in contingencies where fundamental and established or otherwise inexpressible laws had to be stated. It has been attempted, moreover, to substitute for formal theories their practical content. The same holds for the results of theoretical physics, whose dicta touching elementary molecular processes are ever more strongly influencing the conceptions of kinetics. The results of modern quantum mechanics especially, could only be employed in this manner.

The special presentation opens with the study of homogeneous gas catalysis. This field, formerly very small, has grown extremely rapidly with the investigation of chain reactions. It is full of unanswered questions and is in a state of continual transformation. A cross-section, such as this has come to be, is necessarily limited by time, with the result that many things described in the text as doubtful, are more certainly known today.

In the older field of catalysis in solution, the lines of development have become more stereotyped. Here also, the original literature has been fully consulted, but it became obvious that a comparison of the results of various investigators in this field is rendered more difficult by divergences in their points of view. Nevertheless, endeavor has been made to bring about a compromise, which would allow previous work to help in the formation of a better conception of the problem.

Nearly half of the book is devoted to the subject of heterogeneous catalysis, and here, greatest use could be made of compilations already available. The fundamental questions of activation by the catalyst, which apply equally to homogeneous catalysis, have found the most far-reaching answer in heterogeneous catalysis, and, therefore, together with the structure of the surface, stand in the forefront of our consideration. In this section particularly, a certain subjectivity of standpoint can be excused as essentially unavoidable.

In the last section a short review is given of enzyme catalysis and catalysis in the organism, as far as it can be considered from the standpoint of kinetics and is kinetically connected with catalysis in vitro. Naturally, no effective review of the material can be given in this section, only suggestions and indications; and, above all, it cannot claim any precedence over the books of other authors in this field. With regard to the rôle of catalysis in technology, it was finally decided to forego any such short summary, since it would hardly belong to the logical plan of the book.

[1] These have been incorporated in the text in the English translation. Tr.

Here also, several of the latest special works in German and English (H. Bruckner, T. P. Hilditch, E. K. Rideal, H. S. Taylor) can be consulted.

It is assumed that the reader has a good knowledge of chemistry, is conversant with the principles of physical chemistry, and has some knowledge of physics and elementary mathematics. On this basis, the author hopes he has made this common border region intelligible to biologists as well as to chemists and physicists. May the book furnish whatever physicochemical information is desired to all who are interested in catalysis, either as a special field, or as a sideline from some other field, and may it be of advantage to them. I shall always be thankful to colleagues for possible suggestions, wishes and improvements.

To Dr. U. Heyde and Dr. L. Rudolph, who helped me unstintingly with the literature index, I extend in this place, my heartiest thanks.

GEORG-MARIA SCHWAB.

MUNICH,
June, 1931.

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CHAPTER I

HISTORICAL INTRODUCTION

IT is a rather surprising fact, in view of the very general significance of catalysis in chemical processes, that its recognition does not extend so far back in history and cannot be so closely followed, as chemical knowledge in general. Mankind's oldest chemical experiment, in production of fire, has only joined the list of catalytic reactions by the comparatively recent recognition of the rôle of water vapor in the flame. Apart from flame, therefore, the first catalyses to become known and deliberately carried out were enzyme processes, namely wine-making and the preparation of vinegar from alcoholic liquids; processes in which Nature herself furnished the catalyst to unsuspecting man. Alcoholic fermentation in particular appears quite generally and contemporaneously in the earliest documents of civilization, that is in the time of the Chinese, Assyrians, and Egyptians, but without the latter having perceived its nature in spite of their otherwise good chemical knowledge. The first case in which we find the artificial use of a catalyst, is the well known formation of ether from alcohol and sulphuric acid, alleged to have been discovered by Abu Musa Dschabir (vulgo, Geber, b. 702), although there is now some evidence in the form of authenticated prescriptions in favor of a later date. Here also, however, the nature of the action was not understood; the view was long held that " sulphuric ether " contained sulphur.

It is accordingly all the more astonishing and unexpected that we should find eventually, in the alchemical middle ages, the ideas of catalysis playing a governing rôle in chemical theory. This appears to be characteristic of an epoch in which philosophic and metaphysical doctrines enjoyed precedence over experiment as the source of scientific theory. The Aristotelians saw in what we now call a " material " change, a mere alteration in form, in which the " Materia " of the " Substance " is preserved. From this standpoint, especially when specified by the introduction of principles of Form (the Aristotelian fire, water, air, earth, or the Alchemical salt, sulphur, mercury), a transmutation of the metals appeared, like any other chemical process, to be something natural and an *a priori* possibility. Practices such as the formation of bronze from copper and tin lent color to this view. Since

the tenet " Forma educitur de potentia materiae " [1] (which implies that the change occurs in the direction of a diminution in free energy) prevailed, such mutations, when they can occur at all, are spontaneous. The conception that such processes can be intentionally favored by the addition of a " Substance " (which we would call the catalyst) appears to lie in the close relationship which the chemistry of that time bore to medical science, where it had long been known that medicines assist the endeavors of Nature. It was, therefore, to be expected that the same substance, the " Philosophers' Stone " or the " Quinta essentia," should have the property of transforming base metals into gold, as well as conferring good health and long life.

Thus, we can see the modern definition of a catalyst contained in the ideas of the Philosophers' Stone. Again, the further criterion of catalysis, that any given small quantity of a catalyst can bring about any desired large change, is reflected with remarkable exactness in the working directions of the alchemists. For instance, a preparation of gold by Paracelsus [2] is described as follows: " One day he declared: ' Frantz, we have no money, give me some Rhenish florins,' and said, ' Go to the apothecary's shop, have a pound of mercury weighed out to you and bring it hither to me.' I did that, giving it to him together with the remaining money (at that time mercury was not expensive). Then he placed four tiles together on the hearth, so that the air could circulate underneath a trifle, and poured the mercury into a crucible, put it between the four tiles, commanded me to throw charcoal around it, and after that likewise commanded a lively fire and the addition of more charcoal. Then we allowed it to proceed gradually and went indoors, because it was cold at the time. After some time he said: ' Our servus fugitivus may wish to escape us outside, we must see what it is doing.' As we approached, it was already beginning to smoke and fly away. Then he said: ' Look, take this pestle in the tongs and hold it in the crucible for a short time, it will soon melt.' When this had happened, he said: ' Take out the tongs again, cover the crucible, give it a good fire, and allow it to stand.' Then we went away inside, leaving the contents of the crucible alone. After half an hour, he said: ' Indeed, we must see what God has given us. Lift the cover from the crucible.' I did that, but the fire had completely gone out and everything in the crucible stood still. He said: ' How does it look? ' I replied, ' It looks yellow like gold.' ' Yes,' said he, ' it should be gold, too.' I took it out. It was gold . . . *It weighed a pound all but half*

[1] F. Struntz, *Albertus Magnus*, p. 86, Menschen, Völker, Zeiten, **15**, Vienna and Leipzig.

[2] F. Spunda, *Paracelsus*, p. 91, Menschen, Völker, Zeiten, **6**, Vienna and Leipzig.

an ounce . . . It (the catalyst) *was a small pestle about the size of an average hazelnut*, set in red sealing wax . . ."

And on another page [3]: " Theophrastus sent his waiting man, whom he had taken into his service a few days before, to deliver to the steward a small piece of paper inside of which was a small blood-red powder, with the command that he was to pour it into the molten lead in the crucible and stir well . . . Then he let his host beg that he might take this manufactured gold to the Master of the Mint of the place, who . . . paid him *several thousand guilders* for it."

These examples suffice to show the remarkable manner in which the mediaeval fantasies of the Philosophers' Stone corresponded to our present-day knowledge of catalysts. They are suggestive of an allegory of the many thousand guilders gained today through catalytic reactions.

The ideas of catalysis already dormant in the dreams of the alchemists were first awakened to practical life, however, through the origination towards the end of the 18th century, of exact chemical inquiry. Then, following the deepened insight into chemistry, the number of catalytic reactions, known as such, rapidly increased. In 1781, Parmentier discovered the saccharification of starch by acids, subsequently investigated, among others, especially by Döbereiner. Eventually, in 1812, its significance was fully understood by Kirchhoff. De Saussure, in the case of the saccharification of gluten, was the first to conceive the idea of acceleration of reaction in 1818, but he remained, as we shall see, for a long time without adherent or successor. At that time also, the first investigations of surface catalysis were carried out: Van Marum investigated the dehydrogenation of alcohol by metals in 1796, and Deimann, van Troostwijk, Lawrenberg, and Bond studied its dehydration by clay; between 1817 and 1823 both Davy and Döbereiner investigated the phenomena of the glowing of metals in mixtures of air and combustible gases (Döbereiner's tinder box). In 1825, Döbereiner discovered the catalysis of the decomposition of potassium chlorate by manganese dioxide, Thenard the decomposition of ammonia by metals in 1813 and later that of hydrogen peroxide in 1818, while Faraday performed the first experiments on the catalytic synthesis of ammonia from the elements in 1825, experiments, however, which are, it is true, not entirely unequivocal.[3a]

These were the oldest and most important of a large number of separate data, that had to be known, in order that Berzelius might be able, about 1836,

[3] F. Spunda, p. 102, *loc. cit.*

[3a] See Gmelin, *Hand. d. Anorg. Chem.*, Section on Nitrogen and Ammonia.

to apply his gifted synthetic touch to their classification under a new collective idea, namely that of " Catalysis." He writes:[4] " As long as . . . their mutual connection (that of the ' new power of inducing chemical activity ' with the ' general electrochemical relationships of matter.' Author) remains obscure, *it facilitates our inquiries,* to consider it for the present as a force in itself, just as it facilitates our discussion of it if we have a special name for it. I shall, therefore, call it, to make use of a derivation well known in chemistry, the Catalytic Force of Bodies and the decomposition which it produces, Catalysis . . . "

" The catalytic force appears essentially to consist in this, that bodies, through their mere presence, not through their affinity, have the power to awaken affinities dormant at this temperature and, as a consequence of this, the elements in a compound substance arrange themselves in such other relationships as bring about a greater electrochemical neutralization." Some sentences follow, in which were clearly raised the problems of what we now call selective catalysis.

One cannot help thinking that in this concept of a " catalytic force " which " awakens the dormant affinities " (potentia materiae of the middle ages) the latent alchemical idea came to fruition, to a development which was quite consciously conceived, in the sense of the most modern scientific theory, as a purely heuristic formulation " a facilitation of our investigations and discussions." This aim has certainly been realized, for although we cannot, as yet, even comprehend all catalytic phenomena in one functional system, the great heuristic achievement of Berzelius has nevertheless been the starting point of scientific interest in catalysis and its investigation.

About the same time, Mitscherlich [5] grouped a series of such phenomena under the name " Contact Action," although not without some attempt at a mechanistic explanation. The immediate result of advancing these ideas was certainly not the origination of a new direction of experimental inquiry, but a long epoch, filled with attempts to attribute a general " explanation " to the new idea so as to interpret the " catalytic force " theoretically. Following Liebig's powerful opposition to the " catalytic force " (which he assessed too highly as an attempt at an explanation), all kinds of different theories of catalysis were expressed during the next sixty years, for the most part conceptions, such as those of molecular fields of force or intermediate reactions, which have later largely proved to be correct. However, since it has been shown more recently that the

[4] Berzelius, *Jahresber. Chem.*, **15**, 237 (1836).

[5] Mitscherlich, *Liebig's Ann.*, **44**, 186 (1842).

search after one comprehensive theory was bound to remain unfruitful, real increases in knowledge in this way have been small.[5a]

This situation was changed for the first time, when, at the end of the 19th century, the young science of physical chemistry became master of the still enigmatical concept and brought the quantitative method to bear in its elucidation. W. Ostwald was successful in this respect, in that he introduced the *velocity* of the change as a *measure* of catalytic action. The old concept, now clarified by physical chemistry, that, in catalytic reactions, it is only already existing affinities which become effective, together with the consideration, that, fundamentally, these can also act without a catalyst, but very much more slowly, led Ostwald [6] to his classical definition of catalysis: " *A catalyst is any substance which alters the velocity of a chemical reaction without appearing in the end products.*"

The theory which Berzelius had arrived at empirically was overwhelmed in one blow by this introduction of reaction velocity into the problem, which, through its stated relationship to a measurable quantity, became the object of new and more exact inquiry. Every investigation of catalytic phenomena, to which we owe our more exact knowledge of the present day, dates from this moment.

It has turned out that the reservation in the Ostwald definition, that the catalyst does not appear in the end product and therefore does not enter into the equation of the reaction, had to be made more precise. Thus Bredig [7] remarks: " *According to this, the so-called catalysts can remain unaltered or also become altered themselves, but in the latter case they are still only to be considered as catalysts, when no stoichiometric whole number relationship exists between the amount of the so-called catalyst eventually changed and the amounts of the other substances, the so-called substrate, that are converted.*"

And Abel [8] even goes so far as to postulate: " Not substances, but only reactions are catalyzed." That this last statement does not contradict the Ostwald definition, is evident from what follows. However, in this last epoch, progress has proceeded not so much from the assertion of a strict definition, once a fruitful one was found, but rather in that we have obtained the velocity relationships of a very large number of catalyses

[5a] See A. Mittasch ' Berzelius und die Katalyse, Leipzig, *Akad. Verl. Ges.* 1935; also, *Naturwiss.*, **21**, 729 (1933); also, Mittasch, " Uber die katalytischen Verursachung in biologischen Geschehen " Berlin, 1935; Mittasch and Theis ' Von Davy und Döbereiner bis Deacon, Berlin 1932.

[6] W. Ostwald, *Physik. Z.*, **3**, 313 (1902).

[7] G. Bredig, *Ulmann's Enzykl. techn. Chem.*, **6**, 670 (1909).

[8] E. Abel, *Z. Elektrochem.*, **19**, 933 (1913).

from an abundance of experimental work, and have thereby obtained insight into their mechanism.

The result has been that, today, we have before us not a uniform theory of catalysis, but a field of which the attraction lies in the variety with which the different principles operate, partly in different processes, partly in one and the same process. With the growing penetration of Science, Technology has increasingly made use of the possibilities thus offered and, in its turn, has placed problems of a special, but quite fundamental nature, before Science. The " Riddle of Catalysis " is in general still unsolved; most of all, we do not know *why* a substance catalyzes a reaction. However, we often know *how* it happens, and see in this knowledge our mastery and the goal of the investigation.

Owing to the many-sidedness of the phenomenon, specialization has occurred, and the various divisions have frequently drifted apart. The more recent development of these will not be included in this historical section, in which it was only a question of following the development of the catalytic idea to its exact definition.

CHAPTER II

GENERAL INTRODUCTION

THE somewhat pessimistic conclusion which we have already reached from the present condition of our knowledge, that there is not a single mechanism of catalysis, naturally does not exclude the possibility that a quite general correlation of the pertinent phenomena, covering a whole series of items, can be given. Such general features will be stated first here so that they may be referred to later. Something also must here be prefaced with respect to the material nature of the catalyst in which is involved the most advantageous exposition of the available definitions.

Catalysis by Substances: In agreement with Ostwald (see p. 5), we regard catalysis as the action of a *substance* which alters the reaction velocity, whereby the connection between catalysis and *substance* is emphasized. In accordance with this idea, we shall consider only those changes brought about by material catalysts, and exclude accelerations produced by introduction of energy in the form of the electric discharge, irradiation by light, collisions and so on, even when a spontaneously occurring process is concerned. In particular, the acceleration produced by increase of temperature does not come under the heading of catalysis, since it is common to all reactions, whether spontaneous or catalyzed.

Positive and Negative Catalysis: The substances which we are going to discuss, produce an alteration in the velocity of a reaction which can be either positive or negative in character, signifying acceleration or retardation. We speak, accordingly, of " positive catalysis " or simply of " catalysis," and of " negative catalysis " or " inhibition." It has often been proposed to exclude the latter from the definition of catalysis, as a phenomenon having a subordinate or secondary explanation, because it is difficult to understand how a substance could " suppress " an already existing possibility of reaction by its mere presence. In conformity with our definition we cannot do this. Further, among the many various mechanisms of positive catalysis, there are some, of which negative catalysis forms so much the direct antithesis, that their separation from one another

would do violence to the facts, as will appear in the several chapters concerned.

Furthermore, the question has arisen, and recently in a distinguished quarter,[10] whether actually (positive) catalysis always implies an " alteration " of velocity, in the sense that the reaction concerned already possessed, in the absence of a catalyst, a finite velocity. Cases are accumulating of reactions effected by catalysts, e.g., in technology or in the organism which do *not* appear to occur *at all* in the same substrate (the initial reactants in a catalytic reaction are called the substrate) *without* the catalyst, and it has been suggested therefore that catalysts possess the ability to *produce new reactions.*

This is no doubt permissible as far as the actual experimental data are concerned, although an alteration of the Ostwald definition on these grounds seems to be avoidable. When we say that a reaction does not occur spontaneously, i.e., without a catalyst, we have two cases to distinguish. In the first place, it may concern a process which cannot take place for thermodynamic reasons, because it would entail a change in the system away from equilibrium. Even when it is possible to effect such a process in the presence of another substance (e.g., the formation of ozone from oxygen by white phosphorus) it will not be described as " catalysis." We shall return to this point later. On the other hand, if the reaction proceeds of its own accord, i.e., tends to establish an equilibrium, the statement that it does not occur spontaneously can only be taken in a quantitative sense, and, in principle, one can always attribute to such processes an immeasurably small reaction velocity, which is raised to measurable proportions catalytically. Thus, it is impossible to draw a sharp distinction between the hydrogen-chlorine combination, which occurs in the space of months, and the hydrogen-oxygen combination, where no reaction is observable. Likewise, the directing of a system along a " new " course of reaction by a catalyst, is simply due to an increase in the velocity to measurable magnitude along a path which was already possible.

We have now to take up the consideration of that property of reactions which is subject to variation, namely their velocity. However, we cannot undertake to give here a detailed treatment of the theory of chemical reaction velocity as far as it concerns the systems later to be discussed; reference should be made to the standard textbooks on the subject (Eggert [11]

[10] R. Willstätter, *Osterr. Chem. Ztg.*, **32**, Nr 13 (1929); Faraday Lecture, 1927, *Verein. d. Freunde d. Techn. Hochsh.* Darmstadt, **1927**, H.9.

[11] J. Eggert, *Lehrb. d. phys. Chem.*, 2nd ed. Leipzig, 1930.

and especially Hinshelwood [12]). We can only recall some of the fundamental facts, in order later to be able to refer to them in detail.

Simple and Composite Reactions: First of all we have to distinguish between simple and composite reactions. This can often be accomplished with the aid of the " velocity equation," i.e., the dependence of velocity on the concentration of the reactants. Then again, in composite reactions we have to distinguish between successive and simultaneous reactions, e.g.:

Successive reactions	(1)	$A + B = C$
	(2)	$C + D = E$
Simultaneous reactions	(1)	$A + B = C$
	(2)	$A + D = E$

Those reactions which are not capable of further resolution and, therefore, represent the actual molecular processes, are called elementary reactions or primary reactions. They can be either addition reactions ($A + B = AB$) or (more probably) substitution reactions ($A + BC = AB + C$), and for the most part they are bimolecular, since termolecular reactions (triple collisions) are rare. Some elementary reactions appear to be unimolecular, particularly decompositions of relatively large molecules.

The Velocity of Simple Reactions: The general velocity equation is of the form:

$$dx/dt = k \cdot f(c_1, c_2 \ldots).$$

In accordance with the preceding remarks, in the case of primary reactions, the concentration function, $f(c)$, must always be an integral power of c, usually the first* (reaction of the first order), or the second, or the product of two different concentrations (reaction of the second order).

According to the theory of Arrhenius,[12a] as modified by later studies, in any reacting system only certain " active " molecules possessing a minimum energy, q, actually take part in the reaction, and the velocity of the change is directly proportional to the concentration of these active molecules, which is governed by Maxwell's distribution law. If we assume that the total energy in the system is distributed by collisions between the constituent

[12] C. N. Hinshelwood, Kinetics of Chemical Change in Gaseous Systems, 2nd. ed. Oxford, 1929. 3rd edition, 1933. See also L. Kassel, Kinetics of Homogeneous Gas Reactions, Chem. Catalog Co., New York, 1932.

* We classify all reactions which give this function, including composite reactions, as " first order"; the term " unimolecular reactions " will be applied to elementary reactions which are actually confined to one molecule.

[12a] S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

molecules, we obtain for the velocity constant:

$$k = Z \cdot e^{-q/RT}$$

where Z is the number of collisions in unit time and T the absolute temperature. The value of q, has a dominant influence on the reaction velocity. The smaller q is, the faster the reaction at the given temperature. It is the energy necessary for reaction, the activation energy. It has nothing to do with the heat of reaction since often even exothermic reactions require an activation energy. Only in ' dynamically homologous ' reactions of substances, constitutively very similar, is there a relation to this extent that affinity and velocity run parallel, presumably because the heat of reaction and activation energy change similarly in such series.[12b] In all other cases, and especially in velocities which are changed by catalysis, the activation energy is a property of the molecular structure of the reactants which is not determined by thermodynamics (see p. 166).

In the case of most simple bimolecular reactions, the above formula represents the experimental results with considerable accuracy. However, although many reactions ultimately appear to be bimolecular, a certain number, usually decompositions, exhibit first order properties over a wide range of concentrations. They have not been found to be composite, at least in the ordinary sense, and it is assumed that they consist of unimolecular elementary processes. If such elementary processes occur immediately the centrifugal force due to the rotation of the molecule exceeds a certain value, we should expect the reaction velocity to be dependent on the rate at which the Maxwellian distribution is re-established. Actually, we find the velocity of a unimolecular reaction to be independent of the collision frequency over a wide range. It was suggested by Lindemann [12c] that this difficulty might be surmounted if we assume that the activated molecule does not dissociate until a suitable arrangement of the internal energy has been attained, and that, in the case of unimolecular reactions, this process takes longer than the time necessary for the re-establishment of the Maxwell distribution. Lindemann pointed out that his theory required unimolecular reactions to become bimolecular at low pressures owing to the decreased rate of activation by collision. This property was later established as characteristic of practically all unimolecular reactions. The general equation for the velocity constant of a unimolecular reaction is therefore of the form:

$$k = \text{const. } e^{-q/RT}$$

[12b] Dimroth, *Z. angew. Chem.*, **46**, 571 (1933).

[12c] F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 599 (1922).

The so-called temperature independent factor ' const.' contains several different magnitudes. The components which are temperature independent or nearly so are: the probability that the molecule contains the energy q, therefore a function of the degrees of freedom of translation, rotation and especially of vibration; the probability that this energy goes over by internal vibrations to the bond which is to be broken; and finally the probability that, with a given energy in the bond, it will be broken.

The Velocity of Composite Reactions: We find in practice, however, that most reactions, especially catalytic reactions, are composite and do not belong to these simple types. The study of such processes has been greatly facilitated by the application of the principle of the *independent co-existence* of separate elementary reactions. Nevertheless, while the study of simultaneous reactions thus becomes comparatively simple, successive reactions still present considerable difficulty. It is obvious, first of all, that the collective process must be limited by the *slowest* reaction in a sequence which is " velocity determining " because the other reactions are obliged to wait for it. The observation that unimolecular gas reactions become bimolecular at low pressures owing to the process of activation by collision becoming velocity determining, is an illustration of this point. Particular types of successive reactions, especially those in which the first step is a reversible equilibrium, will be discussed in detail later.

The following general principle may be mentioned here: when the reaction has reached a stationary state, the number of molecules of each intermediate stage arising in unit time must be the same as the number disappearing; the *concentration of the intermediate stages is stationary* or the sum of the probabilities of their disappearance is unity (see p. 51). This assumption is always true when the intermediate products are not very stable, that is to say, when ' at least one of the changes which consume the intermediate substance has a velocity constant which is so large that, were it multiplied by a measurable concentration, it would give an immeasurably large reaction velocity.' [12d] In other cases the reaction will not be stationary, but occur autocatalytically or explosively.

This principle is of particular importance in the case of the so-called *chain reactions*, i.e., exothermic processes in which the end products are associated with the production of so much energy that fresh reactant molecules are activated and the same series of reactions is repeated. The activation can be accomplished either by a direct transfer of energy from the reaction product to the initial material (energy chains) or by the intermediate forma-

[12d] M. Bodenstein, Trabajos del IX Congreso Internacional de Quimica Pura y Aplicada, II (1933).

tion of energy-rich, reactive intermediate substances (material chains). Every chain reaction which has attained a stationary velocity must involve some particular elementary process which breaks the chains, since otherwise explosion would ensue. Under these circumstances, therefore, the number of chain links produced from *one* activation, i.e., the chain length, is finite.

The application of the principle of the independent co-existence of primary reactions and the principle of the stationary concentration of intermediate states, to the study of complex chain processes is chiefly due to Bodenstein and his collaborators. By this means it is possible to calculate the velocity equation corresponding to some proposed chain mechanism and to compare this with the experimental results. The following example will serve as an illustration:

$$\begin{aligned}
&1. \quad A \xrightarrow{k_1} A', \\
&2. \quad A' \xrightarrow{k_2} A, \\
&3. \quad A' + B \xrightarrow{k_3} AB', \\
&4. \quad A + AB' \xrightarrow{k_4} A' + AB, \quad \text{(chain propagating)} \\
&5. \quad AB' + C \xrightarrow{k_5} AB + C'. \quad \text{(chain breaking)}
\end{aligned}$$

The initial reactants are A, B, and C, the end products AB and C′, and A′ and AB′ are energy-rich intermediate stages. When the reaction has reached a stationary state, the intermediate products will be removed as quickly as they are formed, and:

$$[A]\ k_1 + [A]\ [AB']k_4 = [A']k_2 + [A']\ [B]k_3,$$

$$[A']\ [B]k_3 = [A]\ [AB']k_4 + [AB']\ [C]k_5$$

$$+\frac{d[AB]}{dt} = \frac{[A]^2\ [B]k_1k_3k_4 + [A]\ [B]\ [C]k_1k_3k_5}{[A]k_2k_4 + [C]k_2k_5 + [B]\ [C]k_3k_5}$$

or,

$$= \frac{[A]^2\ [B] + [A]\ [B]\ [C]k_a}{[A]k_b + [C]k_c + [B]\ [C]k_d}$$

Further simplifications can usually be introduced in particular cases, but it is obvious that the velocity equations and constants appertaining to chain reactions are considerably more complicated than in the case of elementary reactions. The concentration functions no longer appear as simple powers and the constants are composite, being made up of the constants of several elementary reactions.

Influence of the Catalyst on Velocity: The foregoing introductory survey of the conditions governing reaction velocity is rather abstract and formal, and will find practical illustration in the individual experiments to be discussed later. It was presented here to avoid having to fit it into scattered places in the book and also to allow us to proceed with our inquiry as to the means by which a catalyst can influence the velocity of a reaction. It is evident that the velocity is unequivocally fixed by the constants and interrelationships of the separate elementary processes. However, it is not necessary to assume that the " catalytic force " is a mysterious action at a distance by which a particular substance brings about an alteration in the constants. We have to suppose, rather, that the catalyst enters directly into the mechanism of the reaction. Because of the definiteness of the velocity which we have just mentioned, the appearance of new velocities simply means the operation of fresh elementary reactions or of new arrangements between them, with the participation of the catalyst. Thus, it is not so much that the velocity of the old reaction is raised, but that the catalyst creates a new reaction path, which makes possible a greater velocity and this new path is dependent upon the presence of the catalyst, because the latter takes part in the reaction. The requirement that the catalyst, K, should " not appear in the end products of the reaction " is fulfilled by its final regeneration in a manner such as the following:

$$1.\quad A + K \rightarrow AK,$$

$$2.\quad AK + B \rightarrow AB + K,$$

$$\text{Total:}\quad A + B \rightarrow AB \text{ catalyzed by K.}$$

This is an example of catalysis by an *intermediate compound.* Most positive catalyses can be explained in this way. We shall see later what are the conditions which have to be attached to a compound of catalyst and substrate in order that it may be considered as an intermediate compound through which the reaction is effected (p. 72). However, the conception of a " compound " here introduced is not to be taken in a narrow sense. First of all, the intermediate compound may be so unstable that it cannot be isolated, although appearing as an intermediate and stationary stage in successive reactions or chain reactions. Secondly, it does not need to follow stoichiometric laws. Thus, for instance, the whole field of heterogeneous catalysis concerns surface compounds which are generally neither stoichiometric nor separable. If the concept of the intermediate compound be thus understood, it will be found to be the most fruitful basis for the explanation of the majority of catalytic processes.

Catalysis and Activation Energy: Why is the reaction faster in the presence of a catalyst, or, in the case of successive reactions, why is the slowest of the catalyzed reactions faster than the uncatalyzed reaction? The alteration of the constant factor in the unimolecular equation, or of Z in the bimolecular equation does not have much effect; on the other hand, a *diminution in the energy of activation*, q, means, according to the formula, a large increase in velocity. Let us visualize our reaction system as having to pass over an " energy hill " of height q before chemical change can occur. The catalyst can be imagined as an experienced guide under whose leadership a path is found leading into the opposite valley, without it being necessary to climb the whole of the height, q. Under such circumstances, the catalyzed change will proceed faster. It should be emphasized, however, that while this mechanism is certainly the most frequent, it is not the only one.

Constancy of Catalyst Concentration: We speak of " ideal catalysis " when the amount of the catalyst remaining after the reaction is unaltered. In many current definitions, this is regarded as the essential characteristic of catalysis. However, it appears that, strictly speaking, this need not be the case. Reactions which involve the catalyst must all lead to an equilibrium, and even when this is greatly in favor of the unaltered catalyst, a certain amount of the latter still remains bound to the remaining material or is used up; that is, theoretically, the regeneration of K according to the equation $AK + B \rightarrow AB + K$ is not complete. Side reactions in which the catalyst is used up can also appear in the catalyzed system without us having to refrain from describing the main process as catalytic (e.g., the decrease in the concentration of enzymes through their thermal destruction). It became expedient, therefore, to expand the Ostwald definition in the manner adopted by Bredig (p. 5), and we now look upon it as characteristic of catalysis that the amount of catalyst altered bears no definite relationship to the amount of substrate converted in the same time. Thus, the lead chamber process is to be regarded as catalytic, although part of the nitric acid catalyst is lost as nitric oxide, because the amount of the latter depends on the circumstances, and consequently no relation exists between the nitric acid used and the total amount of sulphuric acid produced.

We are now in a better position to understand why Abel (p. 5) stated that catalysis is only produced by reactions, not by substances. This implies that the normal form of catalysis is only exercised by substances which react in some way or other, and that the action of the catalyst should be traced to some intermediate reaction (as Abel could actually do in certain cases, p. 79). This reaction even furnishes energy, so that the thermal energy of activation is reduced.

Catalysis and Free Energy: If, however, the energy furnished by the intermediate reaction is consumed in a total reaction which does not proceed of its own accord, no catalysis occurs, because no energy is released for the work of regenerating the catalyst which has reacted spontaneously. In such cases, there is a definite relationship between the amount of catalyst consumed and the amount of substrate used, contrary to our conception of catalysis. These processes are called " induced " or " coupled " reactions and will be omitted from our discussion. An example is the oxidation of arsenious acid by bromic acid which cannot proceed alone owing to lack of the necessary energy, but takes place in the presence of sulphurous acid, which furnishes the necessary free energy by its spontaneous oxidation. In this way the sulphurous acid is *irreversibly oxidized*, actually to a definite minimum amount determined by energy considerations. Such a process, therefore, is not to be regarded as catalytic.

Nevertheless, the distinction is not sharp. Activation leading to a spontaneous reaction can always be interpreted as a non-spontaneous endothermic initial step and its acceleration by a reaction involving the catalyst can be conceived as an induction of this kind. The distinction is only that a successive exothermic reaction releases enough energy to return the catalyst partly or completely to its original state. Such processes would be considered as catalytic, since here the amount of catalyst consumed depends on the conditions and, from the energetic standpoint, has zero as a limit. If, however, the amount of catalyst used up is commensurable with the substrate, it is not practical to do so. For example, the autoxidation of sulphites or organic molecules by ferrous ions, studied by Wieland and Franke [13] stands on the borderline. Here the reaction itself certainly proceeds of its own accord, but the catalyst is gradually used up in the process. More recently, Richter [13a] has shown that the " induction factor," or the number of sodium sulphite molecules reacting per molecule of ferrous ion oxidized, is of the same order as the chain length in the thermal and photochemical oxidation of sodium sulphite.[13b]

Catalysis and Equilibrium: Another important property of ideal catalysts, which is often included in the definition, arises in this connection, namely, that it *cannot displace the equilibrium.* Since an ideal catalyst is present in the system in the same amount before and after the reaction, work cannot be obtained from its removal and regeneration. Displace-

[13] H. Wieland and W. Franke, *Ann.*, **475**, 19 (1929).

[13a] D. Richter, *Ber.*, **64**, 1240 (1931).

[13b] H. L. J. Bäckström, *J. Am. Chem. Soc.*, **49**, 1460 (1927); *Trans. Faraday Soc.*, **24** 601 (1928).

ment of the equilibrium would require the expenditure of work and, therefore, does not occur.

However, this is only a limiting rule which holds for ideal catalysis. When equilibria are present between catalyst and initial reactants on the one hand and end products on the other, of such a kind that part of the catalyst still remains combined after the reaction, the complete separation of the catalyst may very well require the expenditure of an additional amount of work and displacement of the equilibrium is possible in principle. The remarkable effect of drying agents on the vapor pressures of different liquids, for example, is according to Smits,[14] perhaps to be attributed to this effect. Generally, however, only a vanishingly small amount of the catalyst remains combined and the required independence of the equilibrium is observed.

If the position of equilibrium is fixed, it follows at once from the kinetic theory, that an ideal catalyst must *accelerate the reaction in the same ratio in each direction*, e.g., in the direction of formation and in the direction of decomposition. This is qualitatively fulfilled in practice. Sabatier, [15, 16] Zelinsky and others have shown, in many cases, that hydrogenation catalysts are always equally good dehydrogenation catalysts, and, according to Mittasch and Kuss,[17] the contacts used in ammonia synthesis can also decompose ammonia, and so on.

It appears that this is likewise only a limiting condition, for two reasons. First of all, Abel [18] shows that it again only applies to ideal catalysis, and as soon as an appreciable part of the catalyst is altered due to the reaction, through the presence of new molecular species after the reaction, a difference in the two accelerations is thermodynamically permissible.

In the second place, it is often overlooked that conclusions based upon equilibrium considerations apply *only to the equilibrium itself* or to states infinitesimally removed from it. Thus, the ideal catalyst need only bring about an equal alteration in the velocities at the position of equilibrium; in other circumstances, the forward and back reactions are only accelerated to the same extent when they approach equilibrium. This is illustrated in Fig. 1. The displacement from equilibrium in an endothermic direction is plotted to the right (in any given units of concentration, mol fraction, free energy, and so on) and the exothermic displacement is plotted

[14] A. Smits, *Z. physik. Chem.*, **100**, 477 (1922); **111**, 161 (1924).
[15] P. Sabatier, *Compt. rend.*, **185**, 17 (1927).
[16] P. Sabatier and A. Fernandez, *ibid.*, **185**, 241 (1927).
[17] A. Mittasch and E. Kuss, *Z. Elektrochem.*, **34**, 159 (1928).
[18] E. Abel, *Z. Elektrochem.*, **13**, 555 (1907).

to the left. The velocity in one direction is given above the origin, and in the other direction below. The continuous lines show the uncatalyzed reaction, the dashes refer to the case in which the accelerations produced by the catalyst are the same at every distance, the dotted lines illustrate the forbidden case in which they are different everywhere (displacement

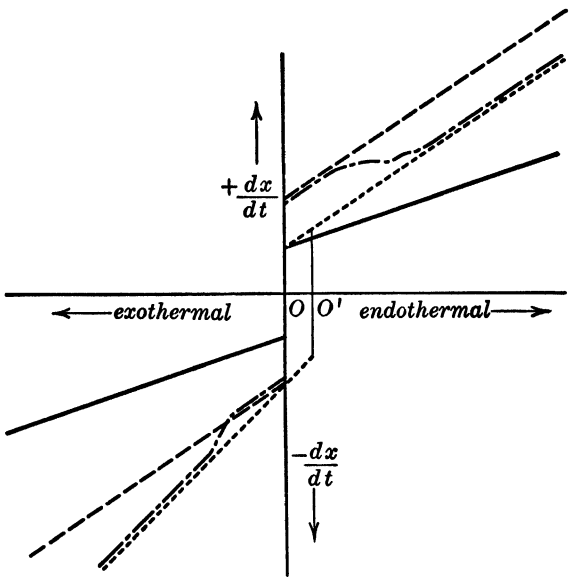


FIG. 1. Catalysis and the Distance from Equilibrium.

of the equilibrium from O to O'), and finally the dot and dash lines represent the permissible case found experimentally, in which the accelerations are equal at the equilibrium point but are different elsewhere.

The latter circumstance actually occurs very frequently. The simple presentation of the " kinetic derivation " of the law of mass action in which the numerator represents the velocity equation of the forward reaction and the denominator the velocity equation of the back reaction, would require the numerator and denominator to be multiplied by the same acceleration factor, to preserve the equilibrium in a catalytic process. In reality, the simple formulation of the velocity equation as a product of concentrations does not hold always by any means, when velocities removed from the equilibrium are considered, and these are, indeed, the only velocities which can be measured experimentally. As a rule, other expressions hold, and, in the case of chain reactions or heterogeneous catalysis, division of the velocity equations does not even give the form

of the mass-action expression of the equilibrium. It is only in special cases that it can be shown that this still holds (Hinshelwood [12]), but usually it cannot be obtained from measurements which are considerably removed from the position of equilibrium (see Baur's discussion of this point [19]). Naturally this does not involve any contradiction of thermodynamics which only refers to equilibrium conditions, where velocity measurements are not practicable (see, e.g., Schwab [20]). In any case, it cannot be claimed under the circumstances, even for ideal catalysis, that both reactions are equally accelerated except at the equilibrium position itself. Inferences drawn from assumptions such as the equal gradation of the properties of the catalyst in opposed reactions (e.g., Mittasch and Kuss [17]) are, therefore, not altogether conclusive, although often justified.

The general conditions relating to catalysis, which have been discussed here, were illustrated by means of catalysis involving intermediate reactions. In so far as they are dependent on thermodynamics, they naturally apply to other forms of catalysis also. It is necessary that this point be noted, since we shall come across other mechanisms such as chain-breaking, chain-lengthening, modification of activity, suppression of diffusion etc., in the succeeding sections. When any difficulties arise, the question will once more be discussed.

Photosensitized Reactions and Catalysis: One means by which new or increased reaction velocity may be brought about has not yet been taken into consideration. Just as the acceleration of reactions by light is not classed among catalyses of reactions proceeding of their own accord, acceleration of photochemical reactions by substances which transmit the light energy is likewise excluded. The numerous cases of such photosensitization will not be discussed, because, here again, the process involved is not spontaneously occurring. (Of course, they can be included equally well in a broader definition of catalysis.) Nevertheless, some account will be taken of the wide field of photochemistry with its valuable information regarding the question of homogeneous catalysis in particular. However, it is only when we are dealing with acceleration of the spontaneous secondary reaction, or dark reaction following the initial photoactivation, that it can be considered to be an example of catalysis in the narrower sense.

Classification: With regard to the arrangement of the material, the usual and most practical classification according to state of aggregation

[19] E. Baur, *Reunion Intern. Chim. phys.*, p. 182, Paris 1928.

[20] G.-M. Schwab, *Erg. exakt. Naturwiss.*, **7**, 292 (1928).

has been followed. Processes in which the catalyst and substrate are present in one and the same phase are called *homogeneous.* Gas reactions are treated first as being simpler; then follow reactions in the liquid phase, i.e., *catalysis in solution,* since we are dealing with a many component system. Homogeneous catalysis in the solid phase is unknown, so that consideration is given in the second place to *heterogeneous* catalysis at phase interfaces, and lastly the intermediate field of *microheterogeneous* catalysis is briefly treated.

This phenomenological classification has been adhered to because the form in which catalytic phenomena appear is very materially affected by the diversity of molecular-kinetic conditions in gases, liquids, surfaces, and colloids. Data, fundamental to the whole subject, must now be discussed in detail in connection with those forms of catalysis with which they have been mainly found and from which they have been most clearly derived. Thus, the laws which hold for chain reactions in the gas phase also apply to solutions, the influence of activity discussed in connection with the latter also holds, *mutatis mutandis,* in the case of heterogeneous catalysis, and the energy relations most successfully worked out in heterogeneous catalysis apply to every form of catalysis.

CHAPTER III

CATALYSIS OF HOMOGENEOUS GAS REACTIONS.

Simple Gas Reactions

Just as the principles of chemical statics can be most clearly expressed in homogeneous gas systems, so can the principles of chemical kinetics be expressed in their simplest form with such reactions and so, of course, also, with catalysis. In no other circumstances do we have such an exact knowledge of the connection between concentrations and other physically measurable quantities (equation of state), or of the frequency of molecular interaction (kinetic theory of gases), and above all, we are never so well informed as to the distribution of energy as in the homogeneous gaseous phase. Whenever we have to deal with condensed phases, the elucidation of the simple elements of a catalytic process is hindered by the reciprocal effects of neighboring molecules, by the development of new degrees of freedom, by solvation, and by topochemical and many other influences.

There are in fact certain homogeneous catalytic processes occurring in the gas phase about whose condition and nature we can even make statements that are in some degree free from hypothesis. It is significant, too, that even in such simple systems, the term " catalysis " appears to be nothing more than a practical general designation for very dissimilar phenomena. In the study of homogeneous catalysis alone, we will make the acquaintance of a whole series of types in which the reaction velocity is modified in entirely different ways.

Catalysis by Intermediate Reactions

From a chemical standpoint, the simplest form of a catalytic process would be that involving intermediate reactions. This means that a new molecule, which is the intermediate stage in the reaction, is formed with the participation of the catalyst and that this intermediate stage both gives the end product and regenerates the catalyst in a subsequent reaction. In order that an acceleration be produced in this less direct way, it is only necessary that the successive reactions occur faster than the simple uncatalyzed reaction; and, since the slowest of the successive reactions determines the velocity, it is obvious that each of the constituent reactions must be faster than the uncatalyzed reaction.

A theoretical discussion of the simplest conceivable case, which, of course, does not correspond to any actual experiment, is given by K. F. Herzfeld. [21] First of all we consider a unimolecular decomposition reaction according to the scheme:

$$1.\quad AB \xrightarrow{k_1} A + B - Q,$$

where Q represents the heat of reaction.

It is catalyzed by X as follows:

$$2.\quad AB + X \xrightarrow{k_2} AX + B \text{ (energy of activation } q_1),$$

$$3.\quad AX \xrightarrow{k_3} A + X - Q_2.$$

Hence the velocity of the uncatalyzed reaction is:

$$v_1 = k_1[AB],$$

and for each part of the catalyzed reaction we have:

$$v_2 = k_2[AB] \cdot [X],$$
$$\text{and } v_3 = k_3[AX].$$

In the stationary state, AX is formed as rapidly as it is used up (see p. 11), so that $v_2 = v_3$. Introducing the total amount of catalyst used $[X'] = [X] + [AX]$, which comprises the free and combined catalyst molecules, it follows from this relation that:

$$[AX] = \frac{k_2[AB]\,[X']}{k_3 + k_2[AB]}.$$

and hence the velocity of the reaction is:

$$v_3 = \frac{k_2 k_3[AB] \cdot [X']}{k_3 + k_2[AB]}.$$

In the first place, we have the important result that *in catalysis by intermediate reactions, the velocity is proportional to the concentration of catalyst employed.* With regard to the dependence of velocity on the concentration of the substrate, two cases are possible (with an intermediate range between them). Either we have $k_3 \gg k_2$ [AB], and reaction 2 determines the velocity, in which case we obtain approximately,

$$v_3 = k_2[AB] \cdot [X'];$$

or conversely, $k_3 \ll k_2[AB]$; under these circumstances, the concentration of the intermediate compound AX increases until all the catalyst is com-

[21] K. F. Herzfeld, *Z. physik. Chem.* **98**, 161 (1921).

bined with the substrate. Further increase in the substrate concentration [AB], has now, of course, no influence on the velocity and we obtain the approximate velocity expression:

$$v_3 = k_3[X'].$$

In accordance with chemical kinetics, we can now write k_1, k_2, and k_3 in the form of temperature functions, thus:

$$k_1 = k_0 \cdot e^{-Q/RT},$$
$$k_2 = Z \cdot e^{-q_1/RT},$$
$$k_3 = k_0 \cdot e^{-Q_2/RT}.$$

Herzfeld here assumes that the molecules in the endothermic reactions 1 and 3 only require the heat of reaction and that additional activation energy is not necessary, whereas the exchange reaction 2 requires a true activation energy. These assumptions agree with observation in a number of reactions in which atoms participate. They do not have general applicability.

In the above equations, Z is the gas kinetic collision number, and k_0 is the factor in the equation of a unimolecular gas reaction, independent of the temperature, which generally is of the order of magnitude of an internal molecular frequency (Polanyi and Wigner [22]). If we now consider the last mentioned case where practically all of the catalyst is fixed, it is clear, since [X'] and [AB] are about the same order of magnitude, that we can only have acceleration of the process ($v_3 > v_1$) when $Q > Q_2$. This corresponds to the well known characteristic that the catalyst provides a new course of reaction (through AX) resulting in a lower energy of activation of the total reaction. Herzfeld shows, moreover, that the acceleration is greatest when Q is about equal to $2Q_2$. It may be compared with the problem of climbing a high wall, which is best accomplished when there is a foothold in the middle, so that neither of the steps is too high.

A more rigid treatment must take into account the back reaction of the intermediate product, if the forward reaction is slow. We therefore make the following addition to Herzfeld's reactions:

$$4.\ AX + B \overset{k'_2}{\rightarrow} AB + X$$

and obtain the equation:

$$v_3 = \frac{k_2 k_3 [AB] \cdot [X']}{k_3 + k_2[B] + k_2[AB]}.$$

As long as the velocity of the back reaction is not too great, the same remarks apply here as in the former case. If the back reaction becomes con-

[22] M. Polanyi and E. Wigner, *Z. physik. Chem.*, A 139, 439 (1928).

siderable the equilibrium between free catalyst (X) and bound catalyst (AX) is displaced in favor of free catalyst. This means, in the first place,

$$[X] = [X'],$$

and, further, a large equilibrium constant k'_2/k_2 which, owing to the equality in order of magnitude of [AB] and [B], leads to

$$k'_2[B] \gg k_2[AB]$$

whence it follows that:

$$v_3 = \frac{k_2 k_3\,[AB]\cdot[X]}{k_2[B] + k_3}.$$

We shall make use of this formulation later. Besides the dissociation reaction $AB \rightarrow A + B$, Herzfeld has treated the exchange reaction $AB + C = AC + B$ in a similar manner and reached analogous conclusions. His theory of successive catalysis will be employed later in another connection.

If we now inquire, however, how this simple and obvious kind of catalytic acceleration stands in relation to experiment, it is found, rather surprisingly, that *this type hardly ever occurs in homogeneous gas reactions* (Hinshelwood [23]): The reason is that, in a gaseous reaction, a third body can seldom be found that will form an intermediate compound with the substrate and provide a conveniently situated energy level besides. On the other hand, it is much more probable in solution, where the energy levels are not so sharp owing to the influence of the solvent, and where the latter can form various unstable ternary compounds. Hence, this kind of catalysis finds its principal application in the field of aqueous solution. (See p. 71.) However, a second and more decisive reason why catalysis by intermediate reactions according to Herzfeld's scheme does not commonly occur in gases, is that very few gaseous reactions proceed in accordance with the simple scheme given on p. 10. These cases are to be valued, rather, as infrequent but very informative exceptions, while by far the majority of gaseous reactions involve a chain mechanism and therefore present much greater difficulties in the study of their modification by catalysts. In connection with the catalysis of chain reactions we shall, of course, still frequently encounter the intermediate reaction mechanism. However, even the induced combustion of carbon monoxide in the water gas reaction, which Hinshelwood [23] regarded as a simple catalysis by an intermediate reaction,

$$\left.\begin{aligned} CO + H_2O &= CO_2 + H_2 \\ H_2 + \tfrac{1}{2}O_2 &= H_2O \end{aligned}\right\},$$

is now considered to be a chain reaction (see p. 42).

[23] C. N. Hinshelwood, *Trans. Faraday Soc.*, **24**, 552 (1928).

A better example of the kind we have been discussing is, according to our present knowledge, the catalysis of the formation of nitrosyl chloride by bromine or nitrogen dioxide, investigated by A. v. Kiss. [24] Formally, the uncatalyzed reaction:

$$1.\ 2NO + Cl_2 \xrightarrow{k_1} 2NOCl,$$

is third order. According to Bodenstein [24a] the reaction occurs via a polymerization of the nitric oxide to double molecules in which equilibrium is established. This, however, does not alter the matter for our purposes. It is immaterial also to the following discussion that, according to Trautz,[25] the reaction occurs in two bimolecular steps with the intermediate formation of $NOCl_2$. The reaction catalyzed by bromine vapor proceeds (in conformity with hypothesis) according to the equations:

$$2.\ 2NO + Br_2 \underset{k'_2}{\overset{k_2}{\rightleftarrows}} 2NOBr,$$

$$3.\ 2NOBr + Cl_2 \xrightarrow{k_3} 2NOCl + Br_2.$$

It is well known that the compound BrCl does not exist, therefore it cannot be introduced as an intermediate. Besides, this assumption would not agree with the observed kinetics. The type of reaction here involved has so far not been given a detailed theoretical treatment, but there is no essential difference if $k_3[Cl_2]$ is introduced into the extended Herzfeld scheme (p. 22) instead of k_3. Summing catalyzed and uncatalyzed reactions (both have measurable velocities) we obtain:

$$\frac{d[NOCl]}{dt} = k_1[NO]^2 \cdot [Cl_2] + \frac{k_2 k_3 [NO]^2 \cdot [Cl_2] \cdot [Br_2]}{k'_2 + k_3[Cl_2]}$$

analogous to p. 22. If $k_3[Cl_2] \gg k_2$, then the velocity is determined by reaction 2:

$$\frac{d[NOCl]}{dt} = k_1[NO]^2 \cdot [Cl_2] + k_2[NO]^2 \cdot [Br_2].$$

In the first place, however, the values of k_2 calculated from the experimental results using this equation are not constant, and, secondly, we should expect to find a much greater acceleration than is measured, since, according to Trautz and Dalal [26] reaction 2 is about 100 times faster than reaction 1.

[24] A. v. Kiss, *Rec. Trav. chim.*, **42**, 112 (1923); **43**, 68, (1924); *Chem. Weekbld.*, **24**, 466 (1927).

[24a] *Helv. Chem. Acta*, **28**, 743 (1935); *Z. physik. Chem.*, A **175**, 294 (1936).

[25] M. Trautz, *Z. anorg. Chem.*, **102**, 98 (1918).

[26] M. Trautz and V. P. Dalal, *Z. anorg. Chem.*, **102**, 149 (1918).

Consequently, the other condition must hold, namely, that $k_3[Cl_2] \ll k_2$. In this case, only a small part of the NOBr present in equilibrium reacts according to reaction 3 and putting $k_2/k'_2 = K_2$ (the equilibrium constant) we obtain:

$$\frac{d[NOCl]}{dt} = k_1[NO]^2 \cdot [Cl_2] + k_3K_2[NO]^2 \cdot [Cl_2] \cdot [Br_2].$$

Substituting measured values of k_1, the factor k_3K_2 actually proves to be constant and we can assume that this scheme gives a satisfactory representation of the reaction.

The catalysis by NO_2 can also be explained in an entirely similar way as follows:

$$1.\ 2NO + Cl_2 \xrightarrow{k_1} 2NOCl,$$

$$2.\ Cl_2 + 2NO_2 \overset{K_2}{\rightleftarrows} 2NO_2Cl,$$

$$3.\ 2NO_2Cl + 2NO \xrightarrow{k_3} 2NOCl + 2NO_2,$$

and k_3K_2 is also a good constant here.

Catalysis by Localized Activation

More recently, a class of catalysis has been studied, possibly not very far different from the mechanism just described but not necessarily due to an intermediate reaction and which can best be interpreted on an energy basis. It concerns the directive catalysis of the decomposition of ether and acetaldehyde by halogens and halides, discovered by Glass and Hinshelwood [27] and studied more exactly by Clusius and Hinshelwood.[28] In the absence of catalysts the following decomposition reactions occur:

Di-isopropyl ether,

$$C_3H_7-O-C_3H_7 \rightarrow 3CH_4 + CO + \tfrac{1}{2}C_2H_4 + C;$$

Dimethyl ether,

$$CH_3-O-CH_3 \rightarrow CH_4 + CO + H_2;$$

Diethyl ether,

$$C_2H_5-O-C_2H_5 \rightarrow 2CH_4 + \tfrac{1}{2}C_2H_4 + CO;$$

Methylethyl ether,

$$CH_3-O-C_2H_5 \rightarrow CH_4 + CO + C_2H_4.$$

[27] V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1815 (1929).

[28] K. Clusius and C. N. Hinshelwood, *Z. Elektrochem.*, **36**, 748 (1930); *Proc. Roy. Soc.*, A **128**, 75 (1930).

All the above are unimolecular gas reactions which fulfill the requirements of the Lindemann scheme at normal pressures, i.e., the number of molecules in the high energy state present in equilibrium is constant. Most of these are deactivated by collision and only a small fraction react. The reaction becomes bimolecular at lower pressures because the velocity of the bimolecular activation becomes less and determines the total velocity of the process. At a certain limiting pressure, the calculated velocity of activation must be equal to the measured velocity of reaction and we have accordingly: (compare Hinshelwood[12] and see also Patat. *Z. Elektrochem.*, **42**, 85 (1935)).

$$dx = \frac{Z \cdot (q/RT)^{(n/2-1)}}{(n/2-1)!} e^{-q/RT} \cdot c.$$

Z is the collision number, q the energy of activation and n represents the number of degrees of freedom. According to the above equation, the greater n is, the lower the pressure required for a given rate of activation at constant q. It appears that the comparatively high energy of activation (see further below) required to break the appropriate binding must be distributed over a large number (from 9 to 26) of degrees of freedom (translational, rotational, and particularly vibrational). In these reactions, therefore, the molecule takes up energy in accordance with the equipartition law until it breaks at the weakest bond. This requires the introduction of considerable energy and consequently the reaction begins at a high temperature, 550° in the case of isopropyl ether.

When any of the following substances are added to the gas mixture, however, all of the above ethers decompose at considerably lower temperatures, the accompanying numbers representing the mean relative efficiency.

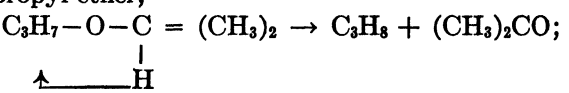
TABLE I—RELATIVE EFFICIENCIES OF HALOGEN CATALYSTS

Iodine	100
isopropyl iodide	70
ethyl iodide	40
methyl iodide	30
hydrogen bromide	20
isopropyl bromide	5
ethyl bromide	4
dibromacetylene	3
chlorides	0

It is evident that the reaction is to be attributed to the free halogen formed by the decomposition of the catalyst; consequently, further experiments were made with iodine vapor.

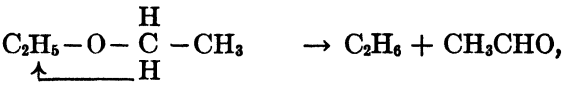
The catalytic decomposition not only begins at a considerably lower temperature (400° in the case of propyl ether), but it also takes a completely different course, e.g.:

Di-isopropyl ether,



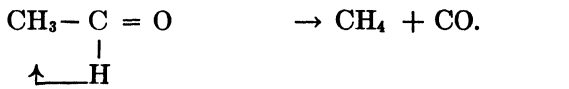
$$C_3H_7-O-C(H)=(CH_3)_2 \rightarrow C_3H_8 + (CH_3)_2CO;$$

Ethyl ether,



$$C_2H_5-O-C(H)(H)-CH_3 \rightarrow C_2H_6 + CH_3CHO,$$

with the successive reaction:



$$CH_3-C(=O)-H \rightarrow CH_4 + CO.$$

It now appears that another part of the molecule is attacked. The carbon atom adjacent to the oxygen always loses a hydrogen atom. All these reactions are bimolecular, i.e., proportional to the product of the concentration of the catalyst and the concentration of the ether. Moreover, the reaction velocity indicates that they occur instantaneously at every collision whence we conclude that both reactants possess only a comparatively small energy of activation distributed over two degrees of (translational?) freedom. The activation energies are given in the following table:

TABLE II — ACTIVATION ENERGIES OF ETHER DECOMPOSITIONS

Substrate	q in kcal. spontaneous	Catalyzed
Dimethyl ether	58	no catalysis
Methylethyl ether	54.5 [1]	38
Diethyl ether	53	34
Di-isopropyl ether	60.5	28.5
Acetaldehyde	45.5	32.5

[1] Corrected according to E. W. Steacie, *J. Chem. Phys.*, **1**, 618 (1933).

The significance of this discovery is fairly clear. The intrinsic strength of the bond broken in the catalytic reaction is greater kinetically than that severed in the spontaneous reaction. Thus, by vibration of the whole molecule (spontaneous reaction) the latter receives its critical energy much more frequently and decomposition occurs with the formation of carbon monox-

ide. In a collision with iodine, however, a specific interaction (chemical or resonance) takes place, in which the available energy (except for a " steric factor " very little different from one) is always transferred to the critical degree of freedom governing the removal of the hydrogen atom, so that this bond is broken before the other, looser, bonds have received sufficient energy. Consequently, since the energy necessary for this reaction is smaller, the temperature can be lower for the same velocity.

We can also consider that the bond broken in the catalyzed reaction was the weakest in the ether-iodine complex. From this point of view, one may perhaps regard the process as an example of catalysis by an intermediate reaction. However, since it is probable that the collision complex reacts during the actual collision period, it is hardly advisable to do so. In any case, these readily interpreted phenomena throw a penetrating light on the mechanism of catalysis by intermediate reactions in that the intermediate substance itself still requires energy of activation. It is very probable that there is a deformative displacement of the relative strengths of the bindings, in the sense that smaller energies of activation become necessary to break the bonds. (See Herzfeld's $Q > Q_2$ on p. 22.)

Modification of the views expressed above may be necessary in view of the quite recent investigations of Rollefson and his co-workers.[28a, b, c] None of these reactions are simple. The iodine used as catalyst is undoubtedly first consumed and then regenerated. Further, the decompositions of the ethers alone occur via aldehyde and the reactions undoubtedly involve, in part, a chain mechanism.

Catalysis by Energy Transference

Phenomena still further removed from the theory of chemical intermediate compounds are known, in which an acceleration of the reaction takes place solely by a transfer of energy from the catalyst to the substrate.

The actual process of energy transference is most obvious in photocatalytic or photosensitized reactions. In these, light energy is taken up by a substance present in the gas mixture which has the specific property of passing this energy to one of the reactant molecules, thus inducing a reaction. For instance, a mixture of hydrogen and mercury vapor becomes highly reducing when illuminated by resonance radiation of wave length 2536 Å, although this light is not absorbed by hydrogen alone.[28d] The re-

[28a] R. F. Faull and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 1755 (1936).
[28b] C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2129 (1936).
[28c] C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2135 (1936).
[28d] G. Cario and J. Franck, *Z. Physik.*, **12**, 162 (1922); **17**, 202 (1923).

ducing action is attributed to hydrogen atoms produced by the transference of energy from the mercury atoms to hydrogen molecules.[28e] Here we do not have an acceleration of an already existing reaction, but the introduction of free energy by the sensitizer imposes an entirely new reaction on the system and for this reason such processes will be excluded from our discussion. However, it is natural that this idea of transference of energy from the catalyst to the substrate should be applied to the catalysis of thermal reactions which take place of their own accord.[29] It can readily be seen that, in principle, such a process must be reversible, and selective activation must be accompanied by selective deactivation in order that the equilibrium, active $\rightleftarrows$ inactive, remain independent of the catalyst added. The most a catalyst can do is to influence the velocity with which this equilibrium is established.

It follows that catalysis of this kind is at once excluded, from such reactions in which the preliminary equilibrium distribution of energy is undisturbed, i.e., from unimolecular reactions of the Lindemann type (see p. 10).

Deviations from this type are now known to exist in two directions. The life of the activated state (time lag between activation and reaction) may be so small that every pair of molecules activated immediately reacts. This happens in bimolecular reactions of simpler molecules such as hydrogen iodide. Here the velocity of activation is certainly the determining influence. However, since it is only such activating collisions in which two substrate molecules are concerned that are effective, a possible additive activation of only one substrate molecule by collision with the catalyst certainly increases the velocity with which the energy equilibrium is established, but not that of the bimolecular reaction. Consequently, bimolecular reactions of the hydrogen iodide type are not susceptible to catalysis by energy transference.

The other possibility, in which a deviation from the Lindemann mechanism is to be found, is that the life of the active molecule may be finite and, at small concentrations, the time between activating and deactivating collisions becomes longer, so that, in the meantime, a large proportion of the active molecules can react. This results in a disturbance of the equilibrium distribution, until the velocity of activation is again the determining factor. This is found to be the case in unimolecular reactions such as decompositions of the molecules of organic vapors, which become bimolecular

[28e] H. S. Taylor and A. L. Marshall, *Z. physik. Chem.*, **120**, 183 (1926); *J. Phys. Chem.*, **30**, 34 (1926).

[29] S. Miyamoto, *Sci. Pap. Inst. Phys. Chem. Res.*, **4**, 257 (1926).

at lower pressures. Since, in this case, only one molecule of the substrate need become activated, it is quite likely that the reaction will be catalyzed by energy transference through activating collisions with a foreign gas.

This effect has actually been found by Hinshelwood and Askey.[30, 31] The specific velocity of the thermal decomposition of dimethyl ether, which is a unimolecular reaction, is known to diminish below a limiting pressure of 400 mm. owing to the velocity of activation becoming the determining process. Within a single experiment, however, the first order character of the reaction is preserved. If activation is produced by collisions between ether molecules, we should expect to find second order characteristics, but only a first order constant is observed.

This can only be explained by the assumption that activation is also produced by collision with one of the products of reaction, so that the second ether molecule can decompose. Experiments on the addition of different gases show that hydrogen is able to do this. The addition of 300 mm. of

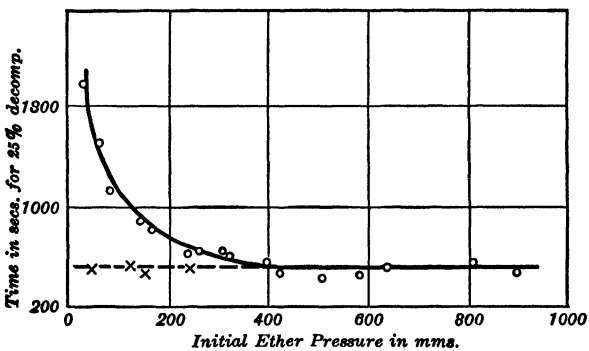


FIG. 2. Quarter-lives in Dimethyl Ether Decomposition (Hinshelwood and Askey) ———— without Hydrogen, - - - - - - - - with Hydrogen.

hydrogen prevents the deviation at low pressure and restores the constant to the normal value that it possesses at higher initial pressures, (crosses in Fig. 2). On the other hand it is significant that the effect is not given by helium, nitrogen or carbon dioxide (which slightly inhibits), and is scarcely noticeable with carbon monoxide.

The same behavior is shown by isopropyl aldehyde,[31] as appears from the half-life times in the accompanying Table III.

[30] C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc.*, A 115, 215 (1927).
[31] C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc.*, A 116, 163 (1927).

TABLE III — INFLUENCE OF HYDROGEN ON ALDEHYDE DECOMPOSITION

Initial Pressure of Aldehyde	Initial Pressure of Hydrogen	Half-life Time
271	0	9′12″
130	0	10′45″
40	0	14′22″
287	407	10′00″
40	211	10′22″
46	402	9′12″
45	610	9′45″

According to Glass and Hinshelwood,[32] hydrogen has the same catalytic effect on the decomposition of methylethyl ether, diethyl ether, n-dipropyl ether, di-isopropyl ether, and methylisopropyl ether. In the case of the latter substance, which decomposes according to the equation:

$$CH_3-O-C_3H_7 \rightarrow CH_4 + CO + C_2H_6,$$

it is evident that the maintenance of first order characteristics cannot be due to hydrogen. Experiments with other added gases show that, here, ethane is also responsible for the activating collisions.

Two points are worthy of note. Firstly, that this kind of catalysis has an upper limit in the velocity of the uncatalyzed reaction at higher pressures (in the above table, there is no change in the velocity between 400 and 600 mm.), and secondly that it is limited to reactions having a region of diminishing velocity in consequence of the governing influence of the activation process. Thus, hydrogen is without effect (excepting a side reaction of another kind) on the decomposition of acetaldehyde, which is an ordinary bimolecular reaction.[31]

Hinshelwood and Askey [30] discuss in detail the question of the origin of this entirely specific property by which hydrogen is able to transfer the energy of the reaction mixture to the ether. In the first place, the hydrogen has the greatest speed and therefore leads *ceteris paribus* to about four times as many collisions as the nitrogen molecule. The ineffective helium atom, which ranks next to hydrogen in the matter of speed, has only three degrees of freedom available for the transport of energy as against five in the case of hydrogen. Since both of these advantages do not quantitatively account for the superiority of hydrogen, the authors consider it conceivable that the ether molecule collects energy specifically from severe collisions with hy-

[32] V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1804 (1929).

drogen. Considering the exceptional position of ethane, one ventures to speculate on the connection of this process with specific resonance phenomena (see p. 44).

More recent experiments also favor this point of view. Especially the researches of Kassel [32a] and Steacie [32b] show that the different ethers cross-activate each other, that is to say, they operate for each other in maintaining unimolecularity and maximum velocity, actually with definite relative activities. Furthermore, quite specific effects have been observed in quite diverse reactions, especially, for example, in the decomposition of nitrous oxide.[32c] The fall in velocity with pressure occurs at pressures of many atmospheres owing to the few degrees of freedom, and is maintained by different foreign gases, including inert gases, in specifically different degrees. Somewhat the same is reported by Schumacher and Sprenger [33] for the thermal decomposition of nitryl chloride. In this case the reaction products are equally as efficient as the reactant in maintaining velocity, nitrogen dioxide alone more effectively and chlorine alone therefore less effectively. Oxygen, nitrogen, carbon monoxide and dioxide are as effective as chlorine; the same is true of hydrogen which, in this case, occupies no special position. The possibility of forecasting energy exchanges occurring on collision is to be foreseen in principle from the measurements of Eucken, Richards and others [33a] on the dispersion of sound in gases. These researches show that transfer of vibrational energy as a preliminary stage in chemical change is in general to be expected between chemically related substances.

Transformation of a Simple Reaction into a Chain Reaction

We have shown so far that, in a catalytic process occurring by intermediate reactions or localized activation, a slow simple reaction is replaced by a faster simple reaction. It is to be expected, however, that catalysis can be brought about by a new reaction, slower in itself, leading to products which can give rise to many new reactions of the same kind in the place of one, with the result that a *chain reaction* is established. Examples of this

[32a] Kassel, *J. Am. Chem. Soc.*, **54**, 3641 (1932).

[32b] Steacie, *J. Phys. Chem.*, **1**, 313 (1933).

[32c] M. Volmer and Frohlich, *Z. physik. Chem.*, B **19**, 89 (1932);
M. Volmer and Bogdan, *Z. physik. Chem.*, B **21**, 257 (1933);
M. Volmer and Briske, *Z. physik. Chem.*, B **25**, 81 (1934).

[33] H. J. Schumacher and Sprenger, *Naturwiss.*, **17**, 997 (1929); *Z. Elektrochem.*, **35**, 653 (1929); *Z. physik. Chem.*, B **12**, 115 (1931).

[33a] Eucken, *Oesterr. Chem. Ztg.*, **20** (1935);
Richards, *J. Phys. Chem.*, **2**, 193, 206 (1934); **4**, 561 (1936).

kind will soon be met. Another possibility would be that one and the same reaction becomes a chain reaction by the addition of a catalyst that initiates the second and third links, etc., perhaps by a specific transference of energy from the end of the first to the beginning of the next separate reaction.

Riesenfeld and Wasmuth [34] have, as we shall see later (p. 45), explained the homogeneous, second order decomposition of ozone as a chain reaction:

1. $O'_3 + O_3 \rightarrow 3O'_2$,
2. $O'_2 + O_3 \rightarrow O'_3 + O_2$ and so on.

The observed acceleration by foreign gases was explained by a specific intermediary effect of the foreign gas molecule in reaction 2. According to Schumacher and Sprenger [35] the assumption of an energy chain in the non-catalyzed reaction is not certainly demanded by the experimental results and compared with simple bimolecular reactions with four degrees of freedom operating, this assumption leads to difficulties. They assume that the chains occur *only* in the presence of foreign gases which take up the energy of the excited molecules O'_2 and utilize it to excite fresh O_3 molecules. Further experiments are required to test the correctness of these assumptions.

It was necessary that this transformation of a simple reaction into a chain reaction be mentioned as it is a theoretically possible form of homogeneous gas catalysis.

Negative Catalysis

The simplest mechanism of negative catalysis, removal of a positive catalyst or removal of one of the reactants by the inhibiting substance,[36] apparently does not occur in gaseous reactions. It is perhaps because of the greater clarity of our knowledge of gaseous systems, that many such influences are easily recognized and then no longer considered as " catalysis " but rather as an alteration of the reacting system. On the other hand, this mechanism will be met with in solution and heterogeneous catalysis.

The only other explanation of negative catalysis in simple gas reactions is the assumption of a specific deactivation. It is obvious, however, that this assumption must be subject to the same reservations as positive catalysis

[34] E. H. Riesenfeld and E. Wasmuth, *Z. physik. Chem.*, A **143**, 397 (1929); B **8**, 314 (1930).

[35] H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, B **6**, 446 (1930), B **11**, 38 (1930).

[36] E. K. Rideal, *Trans. Faraday Soc.*, **24**, 571 (1928).

by activation, namely, that the negative catalyst likewise cannot displace the equilibrium between ordinary and activated molecules. Since it is always the equilibrium or activation velocity that is the decisive factor in thermal reactions and never the deactivation velocity alone (see p. 25), thermal reactions cannot be inhibited in this way (chain reactions are not included in this present discussion; see p. 56).

On the other hand, inhibition is possible as the converse of photosensitization, when the energy of activation is not of thermal origin and therefore does not arise from collisions. In this case, deactivation occurs by collision and produces a change of the stationary state, resulting in inhibition of the reaction. These conditions are found in reactions originated by electrical or more particularly by photochemical means. In the latter connection we shall discuss photodesensitization excluding the question of chain reactions.

Only two examples of this mechanism will be considered. One is the inhibition of the photochemical decomposition of ozone by the addition of "inert" gases first studied by G. B. Kistiakowsky,[37] and more recently and comprehensively by H. J. Schumacher and his collaborators.[37a] Under certain conditions, on illumination with red light, the mechanism is relatively simple (Quantum yields <1.3) and expressible by the reaction sequence

$$O_3 + E = O_2 + O \quad (1)$$

$$O + O_3 = 2O_2 \quad (2)$$

$$O + O_2 + X = O_3 + X \quad (3)$$

The quantum yield is never much greater than 2 and with even moderate oxygen pressures falls below 2. All added gases retard the reaction, in the order He, Ar, N_2, CO_2 and O_2, in which series oxygen is the most efficient. The retarding action is attributable in every case to participation in reaction (3) and the results when the quantum yield is less than 1.3 are given by the kinetic equation

$$\frac{-d[O_3]}{dt} = I_{\text{abs.}} \frac{2k_2[O_3]}{k_2[O_3] + k_3[O_2][X] + k'_3[O_2][X'] + k''_3[O_2][X''] + \ldots}$$

where X, X', X'' . . . are the partial pressures of the third body in reaction (3) each with its specific reaction constant k_3, k'_3 . . .

When the quantum yield rises above 2 it implies a chain which Schumacher

[37] G. B. Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925).

[37a] H. J. Schumacher, *J. Am. Chem. Soc.*, **52**, 2377 (1930); *Z. physik. Chem.*, B **17**, 405 (1932); U. Beretta and H. J. Schumacher, *Z. physik. Chem.*, B **17**, 417 (1932).

represents, for red and ultra-violet illumination, by the reaction scheme

$$O_3 + E = O_2 + O \quad (1)$$
$$O + O_3 = 2O'_2 \quad (2)$$
$$O + O_2 + X = O_3 + X \quad (3)$$
$$O'_2 + O_3 = O_2 + O_2 + O \quad (4)$$
$$O'_2 + O_3 = O_2 + O_3 \quad (5)$$
$$O'_2 + O_2 = 2O_2 \quad (6)$$
$$O'_2 + X = O_2 + X \quad (7)$$

Reaction (4) starts the chain, reactions (5), (6), and (7) are chain breaking mechanisms. The deactivating influence of added gases on reaction (7) is qualitatively the same as that exercised in the three-body reaction (3).

According to Eyber,[38] photochemical decomposition of iron pentacarbonyl proceeds in a similar manner. It may be represented by the following mechanism:

1. $Fe(CO)_5 + E \xrightarrow{k_1} Fe(CO)'_5$
2. $Fe(CO)'_5 + Fe(CO)_5 \xrightarrow{k_2} Fe_2(CO)_9 + CO,$
3. $Fe(CO)'_5 + X \xrightarrow{k_3} Fe(CO)_5 + X'.$

The corresponding kinetic equation is:

$$\frac{-d[Fe(CO)_5]}{dt} = \frac{2 \cdot k_1 \cdot I_{abs.}}{1 + \frac{k_3}{k_2} \cdot \frac{[X]}{[Fe(CO)_5]}}$$

Here, the inhibition, expressed by k_3/k_2, is considerable in the case of water, smaller with carbon monoxide and nitrogen, and unnoticeable in the case of carbon dioxide and argon.

[38] G. Eyber, *Z. physik. Chem.*, A **144**, 1 (1929).

CHAPTER IV

CATALYSIS OF HOMOGENEOUS GAS REACTIONS. II

Chain Reactions

It has already been observed incidentally that positive or negative catalysis is much more likely to occur if the catalyzed reaction is of the chain type rather than a simple reaction. Under the heading of chain reactions, we include those processes which yield the activated starting material or an unstable intermediate, along with the end product. In this way, the same reaction occurs repeatedly and a complete chain of separate processes follows from a single activation (thermal or photochemical). It can either be a material chain such as:

1. $Cl_2 + E = 2Cl$,
2. $Cl + H_2 = HCl + H$,
3. $H + Cl_2 = HCl + Cl$

and so on as in (2), E being one Einstein of light energy, or an energy chain:

1. $N_2O_5 +$ collision energy $\rightarrow N_2O'_5$,
2. $N_2O'_5 \rightarrow N_2O'_4 + \frac{1}{2}O_2$,
3. $N_2O'_4 + N_2O_5 \rightarrow N_2O'_5 + N_2O_4$ and so on as in (2).

(These examples are given without any regard to their actual validity.) A catalyst can have an accelerating or inhibitory effect at the origin of such a chain, thereby influencing the whole of the successive reactions (chain links) simultaneously, as well as being able to catalyze the individual chain links positively or negatively. The possibilities are therefore diverse. Another point arises in this connection. In order to prevent a chain originated by one elementary process from running through the whole system, resulting in an explosion, it must be broken by some means, such as the following:

$$Cl + Cl \rightarrow Cl_2.$$

This increases the possibilities for catalytic action. The chains can be broken by a side reaction (inhibition) at an earlier stage than would otherwise obtain, or the chain breaking process can be retarded, thereby increasing the chain length (acceleration). We shall now discuss the various ways in which these effects can become operative.

1. Positive Catalysis of Chain Reactions

Trace Catalysis: In this connection a phenomenon has first to be considered that is fairly well known, the complete interpretation of which always has caused the greatest difficulties, especially when a comprehensive theory has been sought covering all the phenomena. We refer to observations according to which many reactions attain their 'normal' velocity only if there be present a certain minimal concentration of a foreign substance, especially water. Any excess over these traces of catalyst does not cause any further increase in the velocity. It will be shown that most of such cases belong in the field of chain reactions.

It is necessary to select from the many cases which are difficult to understand those which are quite free from uncertainty in order that it may become clear how far we are dealing with a general phenomenon. Hinshelwood [39] mentions having critically examined a series of eighty-seven researches in which a reaction could be stopped by intensive drying. However, since the list itself was not published, a selection of Tramm's [40] will be given instead.

Solid-solid reactions	CaO, $CuO + SO_3$; $CaO + 2NH_4Cl$;
Solid-gas reactions.....	C, P, $S + O_2$; $CaO + CO_2$; $CaCO_3 + HCl$; $NH_4Cl \rightleftharpoons NH_3 + HCl$; H_2S + salts;
Metal-gas reactions.....	$Na + Cl_2$; Na, $K + O_2$; Na, $Al + HCl$;
Gas reactions	$H_2 + Cl_2$; $H_2 + O_2$; $2NO + O_2$; $(CN)_2 + O_2$; $NH_3 + HCl$.

In the first place, according to Hinshelwood,[39] all those cases in which the reactants are in two different phases can readily be ascribed to adsorption phenomena, and therefore do not tell us anything about the fundamental rôle of water. In Hinshelwood's opinion, the only well authenticated cases in the gas phase were the reactions of $H_2 + Cl_2$ and $2NO + O_2$, and it now appears that both of these may occur in the dry state (see later). He concluded, therefore, that the fundamental uncatalyzed gas reactions need not be doubted. This conclusion is given further support by the fact that the velocity of many reactions, subjected to different degrees of drying, are reproducible and can often be theoretically predicted. The order of the reaction should also be one unit higher than that which is observed if the actual participation of intermixed impurities is necessary.

[39] C. N. Hinshelwood, *Trans. Faraday Soc.*, **24**, 552 (1928).

[40] H. Tramm, *Z. physik. Chem.*, **105**, 356 (1923); see also J. W. Smith, The Effects of Moisture on Physical and Chemical Changes. Longmans, Green and Co., London, 1929.

Nevertheless, the phenomenon of trace catalysis is sufficiently significant that it will be well worth while considering the above and additional cases and to discuss the application of the different explanations possible on the basis of homogeneous chain catalysis.

Baker [41] has investigated the influence of intensive drying with phosphorus pentoxide in about twenty-seven reactions, and the greater part of these experiments were confirmed by Tramm [40] with more modern methods. For example, Baker found that the brown coloration first appears in a mixture of nitric oxide and oxygen after the admission of water. Briner,[42] however, could not reproduce this effect. He also points out that this reaction has a negative temperature coefficient and that according to his experiments, at the temperature of liquid air, where the drying is at least as good as with phosphorus pentoxide, the velocity is sixty times faster than at room temperature. This case must therefore be considered as doubtful.

When a mixture of hydrogen and chlorine is intensively dried with phosphorus pentoxide for four days, less than one-fourth of it, according to Baker, reacts upon exposure to sunlight, while Tramm found none at all. This phenomenon was investigated by Coehn and Tramm [43] and later studied more exactly by Coehn and Jung [44] using liquid air as drying agent. They found that at water vapor pressures below 10^{-5} mm., there is no reaction in visible light of $\lambda > 3000$ Å, but under the same conditions reactions can be brought about by ultra-violet light of $\lambda < 3000$ Å. The reaction proceeds with normal velocity at all water vapor pressures above this limit, in visible light up to $\lambda \backsim 5400$ Å.

Bernreuther and Bodenstein [44a] have subjected these phenomena to a careful investigation and come to the conclusion that no positive catalysis by water vapor is involved, but, on the contrary, that in the drying process traces of impurities are introduced into the gas phase which break the reaction chains so that considerable reaction does not occur. (See later, under negative chain catalysis.)

According to Baker, both the association as well as the dissociation of ammonium chloride can be stopped by intensive drying and this was confirmed later by Tramm. Bodenstein [44b] points out that this observation could not always be confirmed and believes that it can be attributed to a removal, through drying, of condensation nuclei for the solid salt being formed, if,

[41] H. B. Baker, *J. Chem. Soc.*, **65**, 611 (1894).
[42] E. Briner, *J. Chim. Phys.*, **23**, 848 (1926).
[43] A. Coehn and H. Tramm, *Ber.*, **56**, 458 (1923).
[44] A. Coehn and G. Jung, *Z. physik. Chem.*, **110**, 705 (1924).
[44a] F. Bernreuther and M. Bodenstein, *Sitz.-ber. Preuss. Akad. Wiss.* **VI** (1933).
[44b] M. Bodenstein, *Z. physik. Chem.*, B **20**, 451 (1933).

indeed, water drops themselves are not required for the formation of ionic compounds (see later, the effect of the medium in the formation of dissolved organic compounds).

Tramm reports the inhibition of the following reactions by drying: the explosion of detonating gas, the formation of phosgene and the formation of sulphuryl chloride. Rather surprisingly, he found the opposite effect in the photochemical decomposition of carbon dioxide in the ultra-violet. However, Coehn and Spitta [45] showed that water vapor only inhibits above a certain partial pressure, below which it has an accelerating effect. Bodenstein [45a] shows that, in these cases, it is entirely a question of chain reactions which are inhibited by impurities and that, especially, the remarkable behavior of the last-mentioned reaction is readily explained thereby and by the drying process employed. These are not, therefore, cases of real positive catalysis by water.

Dixon [46] discovered the presence of water or hydrides (hydrogen, ether, pentane, hydrogen chloride, and hydrogen sulphide) capable of furnishing water, to be necessary in the ignition of mixtures of carbon monoxide and oxygen, and that the initial velocity of propagation of the explosion wave (and the final, according to experiments of Berthelot and Vieille) [47] rises with the water vapor pressure. We return to these correct observations later.

The formation of nitrosyl chloride catalyzed by bromine (see p. 24) is dependent upon water, according to v. Kiss,[24] but the reaction catalyzed by NO_2 is not, while according to Bodenstein [44b, 48] the formation of phosgene at 200° to 300° in light is inhibited by drying. Here also, however, impurities, introduced through drying, appear to be the cause of inhibition.[44b, 48 and 48a]

An attempt has been made to advance a common explanation of these apparently closely related phenomena, with special reference to the dipole nature of water. It is illuminating that such has not hitherto been attained.

[45] A. Coehn and Th. Spitta, *Z. physik. Chem.*, B **9**, 401 (1930).
[45a] M. Bodenstein, *loc. cit.* and *Z. physik. Chem.*, B **21**, 469 (1933).
[46] H. B. Dixon, *Phil. Trans.*, **175**, 617 (1884).
[47] M. Berthelot and P. Vieille, *Compt. rend.*, **95**, 151 (1882).
[48] M. Bodenstein and A. Plaut, *Z. physik. Chem.*, **110**, 399 (1924);
M. Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927);
H. J. Schumacher, *Z. physik. Chem.*, **129**, 241 (1927);
M. Bodenstein and T. Onoda, *Z. physik. Chem.*, **131**, 153 (1928);
M. Bodenstein, S. Lenher, and C. Wagner, *Z. physik. Chem.*, B **3**, 459 (1929);
H. J. Schumacher and G. Stieger, *Z. physik. Chem.*, B **13**, 157, 169 (1931).
[48a] G. Schultze, *Z. physik. Chem.*, B **5**, 368 (1929).

It is evidently a question of apparently similar processes being effected by quite different causes. Frequently, as we have seen, effects have been ascribed to ' drying ' which have nothing to do with drying. Before this was recognized many efforts at interpretation were made, which, since chain reactions were involved, were drawn from chain theory. We shall return to these presently. Here we may note that nothing now remains of a ' mysterious ' action of water in such reactions.

Intermediate Reactions: The first possibility which we have to consider in connection with the acceleration of chain reactions is again the intermediate chemical reaction. Herzfeld[21] attempted thus to explain the characteristic property of trace catalysis, constant velocity beyond a certain threshold concentration of the catalyst, by intermediate reactions with *two* catalysts. While indeed, his considerations do not refer to chain reactions, they are also valid for these as far as the separate chain links are concerned. As on page 21, the simplest decomposition reaction is again considered, proceeding according to the scheme:

$$1.\ \mathrm{AB} \xrightarrow{k_1} \mathrm{A} + \mathrm{B},$$

and catalyzed as follows:

$$2.\ \mathrm{AB} + \mathrm{X} \xrightarrow{k_2} \mathrm{AX} + \mathrm{B},$$

$$3.\ \mathrm{AX} + \mathrm{Y} \xrightarrow{k_3} \mathrm{AY} + \mathrm{X},$$

$$4.\ \mathrm{AY} \xrightarrow{k_4} \mathrm{A} + \mathrm{Y}.$$

Using the same assumptions as on page 21, we obtain, after a more lengthy calculation, the following limiting cases: (a) Reaction 2 is the fastest and reaction 4 determines the velocity,

$$v_4 = k_4[\mathrm{Y}]',$$

that is to say, in a certain range, the reaction velocity is independent of the one catalyst X, whilst the other, Y, being a constant component of AB appears in place of AB in the equation. If, however, [X′] becomes very small (a threshold concentration), another case arises: (b) Reaction 3 is fastest and reaction 2 determines the velocity:

$$v_4 = k_2[\mathrm{AB}] \cdot [\mathrm{X}'].$$

Below the " threshold " the velocity becomes proportional to the concentration of the catalyst X and remains proportional to the concentration of the substrate. It is evident that the drying effect can be formally represented in this way. We shall see later (p. 46), however, that, in many cases, the

assumed threshold is too low for this to be true. Such calculations are, however, of importance in all those cases where simple proportionality between catalyst concentration and velocity is lacking.

A case which appeared to be an example of chain catalysis was investigated by Daniels, Wulff, and Karrer [49] who believed they had established that nitrogen pentoxide no longer decomposes with its normal velocity in the presence of ozone owing to the removal of nitrogen dioxide by the latter,

$$N_2O_4 + O_3 = N_2O_5 + O_2.$$

Inasmuch as the decomposition of nitrogen pentoxide is a chain reaction according to Sprenger,[50] this would indicate catalysis of the chain by nitrogen dioxide. However, Schumacher and Sprenger [51] were able to show that this is incorrect. In this connection, however, they came across another genuine case of a chain process catalyzed by intermediate chemical reactions, the catalysis of the decomposition of ozone by nitrogen pentoxide,[52] which is known to proceed extremely slowly by itself at room temperatures. In presence of an excess of pentoxide, ozone disappears according to the equation:

$$\frac{dx}{dt} = k[N_2O_5]^{2/3} \cdot [O_3]^{2/3} + k_1[N_2O_5],$$

which can be explained by the following mechanism:

1. $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2,$
2. $NO_2 + O_3 \rightarrow NO_3 + O_2,$
3. $NO_3 + NO_3 \rightarrow 2NO_2 + O_2,$
4. $NO_3 + NO_2 \rightarrow N_2O_5$

and so on according to reaction 1. The chain is broken by reaction 4. The correctness of these assumptions is at once apparent from the fact that the presence of the intermediate compound NO_3 could actually be established spectroscopically, and that the relative values of the constants of the separate reactions lead to the correct energies of activation for the reactions.

Attempts have long been made to explain the catalysis of the combustion of carbon monoxide by water by an intermediate reaction. In this case

[49] F. Daniels, O. Wulff, and S. Karrer, *J. Am. Chem. Soc.*, **44**, 2402 (1922).

[50] G. Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).

[51] H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, A **140**, 281 (1929).

[52] H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, **136**, 77 (1928); B **2**, 267 (1929).

the threshold pressure is about 10^{-3} mm. Thus, Dixon [46] proposed the mechanism

$$CO + H_2O = CO_2 + H_2,$$
$$2H_2 + O_2 = 2H_2O,$$

and could actually prove hydrogen to be present during the explosion. However, Tramm [40] rightly remarked that such evidence is not convincing owing to the invariable existence of the water gas equilibrium after the explosion. In connection with his theory of dehydrogenation, Wieland [53] put forward another mechanism involving intermediate reactions:

$$CO + H_2O = HCOOH,$$
$$HCOOH + \tfrac{1}{2}O_2 = H_2O + CO_2.$$

Formic acid can be directly obtained by the low temperature combustion of carbon monoxide in contact with palladium. However, according to Tramm, its appearance at flame temperatures in any considerable amount (less than 10^{-8} [CO]) is thermodynamically improbable and therefore this mechanism can hardly apply to the flame.

Some indication as to the correct interpretation of the reaction appears to be furnished by the results of modern spectroscopic investigation which Bonhoeffer and Haber [54] have considered in connection with the theory of chain reactions. They favor a chain involving intermediate reactions.

In the absorption spectrum of heated water vapor as well as in that of the hydrogen-oxygen flame, a band system is observed, which, from its form and behavior with varying concentration, can be definitely ascribed to free hydroxyl. This led to an early representation of the hydrogen-oxygen flame as a chain reaction:

1. $O_2 + H_2 + 16$ kcal. $= 2OH$
2. $H_2 + OH = H_2O + OH + 15$ kcal.
3. $2H + O_2 = 2OH + 84$ kcal.
4. $H + OH = H_2O + 115$ kcal.

While all of the above reactions except the first appear to be exothermic (according to absorption spectra data) and therefore likely to proceed rapidly, the mechanism is by no means certain. Reaction 4 breaks the chains. Against this, the historically first formulation of the hydrogen-oxygen chain, all results subsequently obtained with photochemical reactions in systems containing hydrogen and oxygen, by independent investigators such as Taylor, Marshall, Bates, Haber, Farkas, Harteck, Sachsse, Frank-

[53] H. Wieland, *Ber.*, **45**, 679, 2606 (1912).

[54] K. F. Bonhoeffer and F. Haber, *Z. physik. Chem.*, A **137**, 263 (1928).

enburger, Klinghardt and Geib,[54a] indicate the following as the most probable mechanisms.

3. $H + O_2 + M = HO_2 + M + 44$ kcal. (3-body collision)
3a. $HO_2 + H_2 = H_2O + OH + 57$ kcal.
2. $OH + H_2 = H_2O + H + 15$ kcal.
4. $OH + OH = H_2 + O_2 + 112$ kcal. (chain breaking).

The alternative mechanism takes account of the considerable production, in photochemical systems containing hydrogen atoms, of hydrogen peroxide containing more than 90 per cent H_2O_2. A chain mechanism for this reaction sequence was suggested by Taylor and Marshall, of the following form,

3. $H + O_2 + M = HO_2 + M$
3b. $HO_2 + H_2 = H_2O_2 + H$
4a. $HO_2 + HO_2 = H_2O_2 + O_2$
5. $H + H_2O_2 = H_2O + OH.$

The objections raised by Bodenstein to such a mechanism from the standpoint of the inhibitory action of oxygen in the hydrogen-chlorine chain reaction have recently been shown by Kornfeld (*Z. physik. Chem.*, B **35**, 236 (1937)) to be without basis and Bodenstein (Private Communication) has employed this chain to interpret quantitatively, not only the action of oxygen in the hydrogen-chlorine reaction, but also the data of Frankenburger and Klinghardt and those of Bates in the production of hydrogen peroxide from atomic hydrogen in hydrogen-oxygen mixtures.

If we assume in an analogous fashion, that some OH molecules have first of all to be formed in the ignition of moist carbon monoxide-oxygen mixtures, the oxidation of the CO can be formulated as follows:

$$CO + OH = CO_2 + H + 24 \text{ kcal.}$$

Fresh OH molecules are formed according to 3, 3a and 5 thus continuing the chain until it is broken by 4 or 4a. The necessity for the presence of water in these reactions is therefore readily understandable. Further interesting deductions from these considerations, especially with regard to the combustion of hydrocarbons, will only be mentioned in passing, as they are rather far removed from the strict field of catalysis.

In this connection we may also refer to the catalysis of the hydrogen-oxygen combination and ignition by nitrogen dioxide. We shall treat it in more detail when we discuss the theory of explosion reactions (p. 52). It

[54a] Literature references in M. Bodenstein and P. W. Schenck, *Z. physik. Chem.*, B **20** 437 (1933).

may be mentioned here that the catalysis probably occurs through the entrance of the nitrogen dioxide molecule into the stages of the chain,[54b] producing branching of the chain. The energy rich chain carriers H or OH can obviously react with nitrogen dioxide with dissociation of the latter, as, for example,

$$NO_2 + \text{Energy} = NO + O$$

and thereupon

$$O + H_2 = H + OH$$

a process, therefore, which starts two new chains which also can again branch.

Of past efforts to use chain catalysis with intermediate reactions to explain trace catalysis, mention may be made of the interesting, though now untenable, considerations of water vapor catalysis of the hydrogen-chlorine photoreaction. Cochn and Jung [55] attempted to interpret the effects of drying in such a way that, of the two intermediate reactions of the chain,

$$2.\ Cl + H_2 = HCl + H$$
$$3.\ H + Cl_2 = HCl + Cl,$$

reaction 2 could only occur through the agency of water molecules, thus,

$$2a.\ Cl + H_2O = HCl + OH$$
$$2b.\ OH + H_2 = H_2O + H$$

There are no grounds, today, for such an assumption. Effort has been made, however, in abandoning this special mechanism, to ascribe the effect of water in a chain step such as reaction 2 to catalysis by a loose hydrate-like compound $Cl - H_2O$, or to three body collisions.

Both explanations, however, suffered from the difficulty that collisions with water molecules, present in less than sufficient amounts, occur too seldom to produce the enormous reaction velocities observed (see p. 47). In view of these discrepancies, it is very gratifying to record that Bernreuther and Bodenstein [44a] could clear up and explain the whole mysterious effect of drying by other experimental factors than water.

Catalysis of Chains by Resonance: In the catalysis of simple reactions by activation, we saw that, in the few cases where it is thermodynamically possible (see p. 28), the assumption of a specific energy transference has to be introduced to explain, for example, the exceptional position of hydrogen (Hinshelwood and Askey [30]) and other gases (Schumacher and Sprenger [51]).

[54b] R. G. Norrish and J. G. Griffiths, *Proc. Roy. Soc.*, A **139**, 147 (1933); A **152**, 196 (1935).
[55] A. Coehn and G. Jung, *Ber.*, **56**, 696 (1923).

This kind of catalysis probably plays a greater rôle in chain reactions, in which only the activation energy of the primary process is derived from thermal equilibrium. In every successive reaction the activation energy is derived from the previous reaction, since the end product activates the starting material of the next separate process. The thermodynamic restrictions advanced previously (p. 29) naturally do not apply to such a process, and a specific transference of energy from the end product to the new reactant can be effected catalytically by foreign gases. For example, when a chain:

$$1.\quad AB' = A + B',$$

$$2.\quad B' + AB = AB'$$

and so on as reaction 1, is broken by:

$$3.\quad B' = B$$

possibly at the wall or in a side reaction, the intervention of a foreign gas X, detrimental to the chain breaking reaction 3, can lengthen the chain and increase the velocity according to the scheme:

$$1.\quad AB' = A + B',$$

$$2.\quad B' + X = B + X',$$

$$4.\quad X' + AB = X + AB',$$

and so on as reaction 1,

$$3.\quad B' = B.$$

The effect of X is dependent upon the probability with which it takes up energy from B′ and, when X′ has a limited life period, the probability with which it gives up this energy to AB. The tendency nowadays is to consider such energy transferences as resonance phenomena between the systems $B + X'$ and $B' + X$, in the sense of wave mechanics,[38] and the process can be termed resonance catalysis.

Riesenfeld and Wasmuth [34] utilize this conception to explain the acceleration of the velocity of the second order decomposition of ozone by foreign gases which just begins to be perceptible beside the first order reaction at low concentrations (see also Riesenfeld and Schumacher [56]). They assume the following chain (see also p. 33):

$$1.\quad O'_3 + O_3 = 3O'_2,$$

$$2.\quad O'_2 + O_3 = O'_3 + O_2, \text{ and so on as in reaction 1}$$

$$3.\quad O'_2 = O_2,$$

[56] E. H. Riesenfeld and H. J. Schumacher, *Z. physik. Chem.*, A **138**, 268 (1928).

and, for the catalyzed reaction:

$$\begin{aligned} 1.\quad & O'_3 + O_3 = 3O'_2, \\ 2.\quad & O'_2 + X = O_2 + X', \\ 4.\quad & X' + O_3 = X + O'_3, \\ 3.\quad & O'_2 = O_2. \end{aligned}$$

The following gases can function as catalysts:

TABLE IV — EFFICIENCY OF FOREIGN GASES

Gas	CO_2	N_2	A	He	O_2
Relative Efficiency	10	4	3	3	0

The assumption of a reaction chain is introduced because the absolute velocity is 10^6 or 4.10^3 times greater [34, 35] than would be expected in a simple bimolecular reaction according to

$$k = Z \cdot e^{-q/RT}.$$

Schumacher and Sprenger [35] show, indeed, that this discrepancy can also be accounted for if it is assumed that, as in unimolecular reactions, in addition to the translational degrees of freedom, others (in this case three "internal" degrees of freedom) are available for the change. Thus, a chain mechanism is no longer necessary to explain the *spontaneous* reaction. We have already seen (p. 33) however, that Schumacher and Sprenger can only explain the catalyzed reaction by the assumption that resonance with X leads to a chain reaction.

It is natural also that we should consider the effect of water vapor from this standpoint, and it again becomes evident that the water (as on p. 44) interferes in every single chain link. From the general standpoint, it does not matter whether this occurs in the form of a transference of rotational or vibrational energy, or in the form of a genuine chemical reaction in the sense of Coehn and Jung [55] or Franck and Rabinowitsch,[57] for chemical change is also favored by a resonance relationship between the initial and final states, as will be discussed in detail later, in connection with heterogeneous catalysis.

A calculation of Kornfeld [58] reveals, however, a difficulty already mentioned, that the length of the chain as measured, for example, by Kornfeld and Müller,[59] when compared with the duration of a single chain as experi-

[57] J. Franck and E. Rabinowitsch, *Z. Elektrochem.*, **36**, 798 (1930).
[58] G. Kornfeld, *Z. physik. Chem.*, **131**, 97 (1927).
[59] G. Kornfeld and H. Müller, *Z. physik. Chem.*, **117**, 242 (1925).

mentally measured by Weigert and Kellermann [60] would require 10^3 or 10^4 times more collisions of water molecules than are possible with the Coehn value for the threshold concentration. Effort has been made to bridge the gap by the assumption that, for a specific resonance, the ' collision cross section ' of the molecules is enlarged, as is often true in such cases, the collision number being thereby increased. The increase necessary is, however, far beyond that which is usual and this, therefore, is an additional indication that the presumed catalysis by traces of water has no actual reality.

It is therefore also unnecessary as has been done by Semenoff [61] to abandon the molecular kinetic treatment in favor of a wave mechanical treatment of resonance between all the molecules of the reaction space, a procedure hopeless from the practical standpoint.

Catalysis in Chain-Starting: The types of chain catalysis so far described, such as the interposition of intermediate reactions and increasing the velocity of activation, were mostly those found also in the case of simple reactions. Now, however, we have to consider entirely different types of catalytic acceleration, found only in chain reactions, and which are characteristic of the latter. First of all, we have to discuss catalysis which is due to the origination of new reaction chains. In this case, of course, a greater efficiency is to be expected, since a whole chain of successive reactions follows from a single elementary process involving the catalyst.

An example of this kind is the catalysis of the formation and decomposition of phosgene by chlorine atoms. Photochemical researches by Bodenstein and his pupils [48] have demonstrated that the reaction is a chain reaction in both directions, in which process,

$$COCl_2 = CO + Cl_2,$$

the molecule COCl enters as an essential intermediate. The same holds good in the thermal reaction. Now Bodenstein and Plaut [48] found, in agreement with previous work of Christiansen [62] that the thermal formation of phosgene at about 300° obeys the equation:

$$\frac{d[COCl_2]}{dt} = k_1[CO] \cdot [Cl_2] \cdot [Cl_2]^{1/2} - k_2[COCl_2] \cdot [Cl_2]^{1/2},$$

and similarly the decomposition proceeds according to:

$$-\frac{d[COCl_2]}{dt} = k_2[COCl_2] \cdot [Cl_2]^{1/2} - k_1[CO] \cdot [Cl_2] \cdot [Cl_2]^{1/2}$$

[60] F. Weigert and K. Kellermann, *Z. physik. Chem.*, **107**, 1 (1923).
[61] *Z. Physik*, **46**, 109 (1927); **48**, 571 (1928); *Z. physik. Chem.*, B **2**, 161 (1929).
[62] J. Christiansen, *Z. physik. Chem.*, **103**, 99 (1923).

We have, then, to deal with a reaction which does not proceed to completion, and in which every velocity is given by the difference between the positive and negative velocities of formation and decomposition. At equilibrium, the velocity in either direction becomes zero. We observe that, in addition to the reaction components, the factor $[Cl_2]^{1/2}$ enters into both terms on the right hand side of the equations. According to the mass action relation:

$$[Cl]^2 = K[Cl_2],$$

this must mean that chlorine atoms formed by thermal dissociation of the chlorine enter catalytically into the primary process. Chains are originated in this way, just as the photochemical reaction is initiated at room temperatures by chlorine atoms produced photochemically. It is characteristic of this catalytic rôle of the chlorine atoms that they come into the formation and decomposition equations in the same way, so that the position of equilibrium remains uninfluenced.

The catalysis of the decomposition of ozone by chlorine, as explained by Bodenstein, Schumacher and Padelt [63] is an unusually clear case of catalysis of a thermal reaction by the formation of chains. In the absence of chlorine, ozone decomposes comparatively slowly at 50°, when not decomposed heterogeneously by contaminated walls. Chlorine completely arrests the wall reaction, but accelerates the thermal reaction, which proceeds, after an initial induction period, in accordance with the equation:

$$dx/dt = k[Cl_2]^{1/2} \cdot [O_3]^{1/2}.$$

This can be accounted for by the following chain mechanism:

1. $Cl_2 + O_3 = ClO + ClO_2$,
2. $ClO_2 + O_3 = ClO_3 + O_2$,
3. $ClO_3 + O_3 = ClO_2 + 2O_2$ and so on as in 2,
4. $ClO_3 + ClO_3 = Cl_2 + 3O_2$ (which breaks the chain).

Here ClO_2 and ClO_3 are intermediates acting as chain carriers, while ClO decomposes into its elements without chain action. If it is assumed that *every* ClO_2 undergoes reaction 2 and, furthermore, that ClO_3 reacts more readily with ozone according to 3 than with itself according to 4, the above velocity equation is obtained in which

$$k = 2k_3\sqrt{\frac{k_1}{k_4}}.$$

[63] M. Bodenstein, E. Padelt, and H. J. Schumacher, *Z. physik. Chem.*, B 5, 209 (1929).

The scheme is well supported by a variety of facts. In the first place, the induction period indicates that an intermediate product ClO_3 has first actually to be formed. By interrupting an experiment for a certain time and obtaining the decrease in $[ClO_3]$, it was even possible to calculate k_4 and its energy of activation. Furthermore, the values of k_1 and k_3 were obtained from this and from the temperature coefficient of the total reaction, the former being in agreement with the value estimated from the duration of the induction period. The assumption that reaction 2 is very rapid receives direct confirmation from the fact that chlorine dioxide and ozone readily give chlorine hexoxide, the condensation product of ClO_3. Since all the separate velocities are known, the chain length, which is not often obtained in thermal reactions, can be deduced, and is about 10^4 links. We have in this reaction, therefore, an example of a catalytic process in which the mechanism — the formation of the chain intermediate ClO_3 — may be directly observed.

A further, somewhat analogous example of catalysis by the initiation of chains, has been furnished by Hertel.[63a] Chlorine, illuminated with light in the banded region of its absorption spectrum, gives excited molecules, which can be dissociated into atoms by collision with H_2, Cl_2 or HCl (compare Coehn and Jung, p. 44). Chlorine atoms so produced, can then initiate the usual chain reaction:

$$
\begin{aligned}
&1.\ Cl_2 + E = Cl'_2,\\
&2.\ Cl'_2 + M = 2Cl + M,\\
&2.'\ \quad Cl'_2 = Cl_2,\\
&3.\ Cl + H_2 = HCl + H\\
&4.\ H + Cl_2 = HCl + Cl\\
&5.\ \quad Cl = \tfrac{1}{2}Cl_2.
\end{aligned}
$$

The corresponding velocity equation, assuming $[Cl'_2] \propto [Cl_2]$, is:

$$\frac{d[HCl]}{dt} = k_H[H_2] \cdot [Cl_2] \cdot [M],$$

where $[M] = (n[H_2] + p[Cl_2] + q[HCl])$. The ratio $n : p : q$, evaluated experimentally, is equal to $1 : 3 : 0.5$. Hertel attributes the high efficiency of Cl_2 to resonance, HCl being considered to be less effective in this respect, while the relatively high value of n is explained by a chemical reaction:

$$H_2 + Cl'_2 = HCl + H + Cl - 0.2\,\text{kcal. at } 5000\,\text{Å}.$$

[63a] E. Hertel, *Z. physik. Chem.*, B **14**, 443 (1931).

When the chains are very long, the question of the efficiency of small traces of catalyst in originating new chains arises once more, since only one reaction involving the catalyst is required to evoke as many as 10^4 subsequent reactions. Attempts have therefore been made to demonstrate the influence of water upon the primary process in the hydrogen-chlorine reaction.

From the shift of the long wave length limit into the ultra-violet by drying as presumed by Coehn and Jung [44] it might have been concluded that the longer wave lengths did not split chlorine into atoms. Observations, however, of Kornfeld and Steiner [64] and of Kistiakowsky [65] show that drying has no influence on the convergence limit of chlorine, which limit is indicative of dissociation into atoms. Hence, this last interpretation of the effect of drying is also of no significance.

On the other hand, the catalytic initiation of chains appears to offer the key to another kind of trace catalysis in which an " all or nothing law " is obeyed. In such cases, a reaction does not occur at all in the dry gas but proceeds with immeasurable rapidity or explosively in the presence of water. The catalysis of the ignition of explosive mixtures of hydrogen and oxygen (Tramm [40]) and other explosive gas mixtures by water, belong to this type and the combination of ammonia and hydrogen chloride, in particular, shows the same characteristics.

It is necessary, first of all, to find out what will be the conditions for explosion, i.e., for the conversion of a moderate velocity to one which is practically immeasurable. This is most readily obtained from a treatment essentially due to Semenoff,[66] although the basis of the theory had also been given by Cremer.[67]

Let us imagine a chain reaction with any suitable mechanism and let the velocity of the primary activation be ϕ_1. This leads to an active intermediate A. The probability that this reacts further, eventually giving A again in addition to the final product of the reaction, that is, the probability of the chain continuing is w. The probability of the chain being broken by deactivation or by a side reaction is therefore $1-w$. Furthermore, we allow for the possibility of one or more molecules of the intermediate A being sometimes formed along with the reaction product and assume, generally, the formation of p molecules of A per chain link.

[64] G. Kornfeld and W. Steiner, *Z. physik.*, **45**, 325 (1927).

[65] G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **49**, 2194 (1927).

[66] N. Semenoff, *Z. Physik*, **48**, 571 (1928); **46**, 109 (1927); *Z. physik. Chem.*, B **2**, 161 (1929).

[67] E. Cremer, *Z. physik. Chem.*, **128**, 285 (1927).

We have now to calculate the velocity ϕ with which the reaction product D is formed. It consists of a summation of two terms: firstly, the D arising directly from the primary A, with a velocity of formation $\phi_1 w$, and, secondly, the D arising from secondary A. Since, according to the hypothesis, pA are formed along with every D, the velocity of formation of secondary A is equal to wp, and that of the corresponding D becomes ϕpw. We have then:

$$\phi = \phi_1 w + \phi pw$$

$$\phi = \phi_1 \frac{w}{1 - pw}$$

The factor $w/(1-pw)$ evidently represents what we mean by the " chain length." The following considerations have an important bearing on the explosion. As long as pw remains less than one, the velocity is finite, and we observe a slow chain reaction. This means that the formation of new chains is always compensated by the probability of the chain breaking. If, however, $pw \geq 1$, the velocity rather suddenly becomes infinitely great, that is, more chains are formed than are broken in the same time, inflammation occurs, and the reaction goes instantly to completion.

Now w alters with the pressure of the initial material and, of course, generally increases with the latter. It is because of this that there is a lower pressure limit to the explosion of a gaseous mixture, and only a certain range of composition yields inflammable mixtures. An upper pressure limit of the initial reactions means that the reactants act as chain breakers above this limit, for example, by changing the walls of the vessel (Thompson) thus decreasing the value of w. Furthermore, it will be seen that only branched chains can lead to explosion. For, since w, a probability, cannot be greater than unity, pw can only become greater than unity when p is greater than one, that is, when the chains branch. This is the case in the examples considered by Semenoff.[67a] With regard, therefore, to catalysis in chain-starting, we understand principally a process whereby the catalyst causes chains to branch and therefore new branched chains. It is easy to see that a simple increase of the primary chain starters, in other words, an increase of ϕ_1, would increase the reaction velocity but could never furnish the condition for explosion that $pw \geq 1$. (See, however, later paragraphs.)

An observation which has greatly clarified the question of the catalysis of ignition was made by Gibson and Hinshelwood [68] and confirmed by Kopp,

[67a] See also reference 67 of Cremer, and also the extended development of this in Semenoff, Chain Reactions, Oxford University Press, 1935.

[68] C. H. Gibson and C. N. Hinshelwood, *Trans. Faraday Soc.*, **24**, 559 (1928).

Kowalsky, Sagulin and Semenoff.[69] They found that NO_2, like water, facilitates the ignition of hydrogen and oxygen, but that, at each temperature, explosion only occurs within quite definite pressure limits of NO_2. Figure 3 shows the ignition temperature of an explosive mixture of hydrogen and oxygen as a function of the NO_2 pressure. Explosion occurs at all points within the curve but does not take place in the region below the curve.

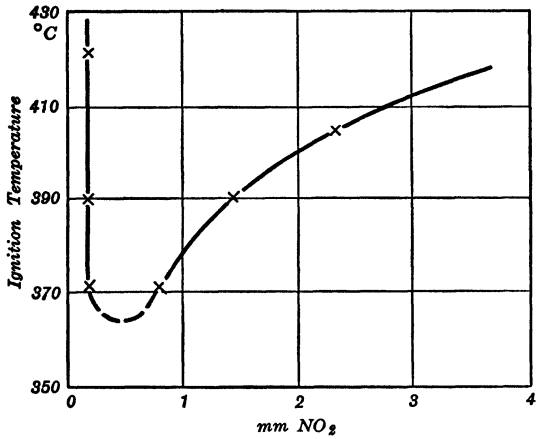


FIG. 3. Influence of NO_2 on the Ignition Temperature of Hydrogen and Oxygen (Gibson and Hinshelwood).

It is very important in this connection that Norrish and Griffiths,[70] and especially Norrish and Foord,[70a] have recently demonstrated that NO_2 accelerates the slow hydrogen-oxygen chain reaction outside the explosion limits and that, for the induction period of this slow reaction, the same laws are obeyed as for the ignition. This shows that the catalysis of the ignition process is actually determined by an effect on p and w, for such an influence must also be observable outside the explosion limits.

Our representation of the whole process is, therefore, as follows: Firstly, the NO_2 increases the chain-branching, p. If we assume the normal chain-branching in the spontaneous explosion above 570° to be represented by the equations:

3b. $H + O_2 = OH + O$

4. $O + H_2 = OH + H$ (at high temperatures, Harteck) the products leading to *two* Haber chains,

3. $H + O_2 = HO_2$

3a. $HO_2 + H_2 = H_2O + OH$

2. $OH + H_2 = H_2O + H$ and so on,

[69] O. Kopp, A. Kowalsky, A. Sagulin, and N. Semenoff, *Z. physik. Chem.*, B **6**, 307 (1929).

[70] R. G. Norrish and J. G. Griffiths, *Proc. Roy. Soc.*, A **139**, 147 (1933).

[70a] R. G. Norrish and S. G. Foord, *Proc. Roy. Soc.*, A **152**, 196 (1935).

an additional catalytic chain-branching will occur according to the equations:

3c. NO_2 + Energy from chains = NO + O

4. O + H_2 = OH + H

reaction 4 again giving two chains which, therefore, in the presence of NO_2, occur more frequently. This additional branching causes the reduction of the explosion temperature to values at which reaction 3 but not 3b occurs, branching occurring therefore by 3c only.

Secondly, NO_2 can also increase ϕ_1, can therefore start quite new chains, by means of the thermally activated reaction 3c. This is especially revealed by the fact that illumination, the photochemical production of reaction 3c, leads to acceleration.

Thirdly, NO_2 also acts as a chain breaker by the mechanism:

5. $NO_2 + O = NO + O_2$.

This leads to the upper limit of the NO_2 pressure. Reactions 3c and 5 were proposed by Schumacher.[71]

It must be observed, in addition, as emphasized by Semenoff,[67a] that, besides these limits between slow and rapid reaction caused by the branching of isothermal chains, a second condition for explosion may be operating. With rapid reaction in any volume element of the gas space the resulting heat may not be conducted away sufficiently rapidly and so the reaction will become *adiabatic* and will lead to the development of an inflammation temperature and a thermal explosion. Such explosions can, naturally, also be favored by an increase of ϕ_1, and thus it has been found that the hydrogen-oxygen explosion can be started by the production of large amounts of chain-carriers. Norrish[71a] has shown that chlorine atoms produced by illumination of admixed chlorine will so act.

$$Cl_2 + h\nu = 2Cl$$
$$Cl + H_2 = HCl + H$$
$$H + O_2 = HO_2 \text{ and so on}$$

Farkas, Haber and Harteck[71b] have demonstrated the effect of admixed ammonia, according to the reaction

$$NH_3 + h\nu = NH_2 + H \text{ and so on,}$$

[71] H. J. Schumacher, *Z. physik. Chem.*, B **10**, 7 (1930).

[71a] R. G. Norrish, *Proc. Roy. Soc.*, A **135**, 335 (1932).

[71b] Farkas, Haber and Harteck, *Z. Elektrochem.* **36**, 711 (1930). *Naturwiss.*, **18**, 266 (1930).

a more detailed study of this effect being later supplied by Taylor and Salley.[71c] Since these phenomena are examples of photosensitization they do not actually belong to the present theme.

The theory of the catalysis of ignition by change in chain-branching permits an easily understandable interpretation of the sharp transition from regions of no reaction to those of rapid reaction. It is, therefore, possible that the catalysis of the formation of ammonium chloride by water, if real, may occur in the same manner.

According to Hinshelwood,[68] if these two types of trace catalysis are actually analogous, the fact that so many processes are catalyzed by water is no longer any reason for assuming that they, or all reactions, are fundamentally catalytic, since hydrogen and oxygen can react in the absence of NO_2. Nevertheless, Hinshelwood [23] considers it conceivable that chain reactions which proceed immediately to completion, i.e., changes of an explosive character always require some kind of catalytic initiation.

Catalysis by Chain-Lengthening: In addition to the acceleration of a chain reaction by intermediate reactions, by the production of new chains chemically, or by resonance, which latter is necessarily specific for definite catalysts and definite reactions, there is still another general principle whereby certain chain reactions can be accelerated by foreign gases of all kinds without any alteration in the scheme of the reaction.

This occurs in the very frequent case in which the reaction which breaks the chain takes place on the wall of the vessel. In these circumstances, the reaction velocity is strongly dependent on the number of links completed between the origin of the chain, and its arrival at the wall there to be broken. Addition of inert gases does not affect the chemical velocity of the chains but their local velocity of propagation is diminished by elastic collisions (Hinshelwood [23]), that is, the diffusion of the active intermediate to the deactivating wall is retarded.

A good example of this kind is the formation of hydrogen bromide studied by Jost and Jung and by Jost.[72] At high pressures, where the chains are broken by three body collisions in the gas phase (p. 57), foreign gases reduce the chain length, because of the greater probability of triple collisions. At low pressures, on the other hand, the same gases accelerate the reaction since recombination in the gas phase is now small in comparison with that taking place at the wall, and diffusion to the wall is diminished by the added

[71c] H. S. Taylor and D. J. Salley, *J. Am. Chem. Soc.*, **55**, 96 (1933).

[72] W. Jost and G. Jung, *Z. physik. Chem.*, B **3**, 83 (1929);
W. Jost, *Z. physik. Chem.*, B **3**, 95 (1929).

gases. The order of the effect given by different gases is that which is to be expected from diffusion considerations.

The thermal reaction between hydrogen and oxygen behaves similarly. It was investigated by Hinshelwood and Thompson [73] in quartz vessels and by Gibson and Hinshelwood [74] in porcelain vessels where it is more reproducible. At temperatures up to about 500° it is a heterogeneous wall reaction of low order (about 1.3). Above about 570°, however, it becomes explosive. Between these temperatures Hinshelwood and his co-workers discovered a *homogeneous* reaction proceeding with measurable rapidity, not accelerated but rather inhibited by increasing the wall. Both the order and the temperature coefficient are considerably higher than in the case of the wall reaction and increase markedly with temperature and pressure.

The last word has undoubtedly not been written concerning the special mechanism of the reaction. Nevertheless, the mechanism discussed in previous pages (pp. 42, 43) becomes increasingly probable. In the temperature range between 500° and 570° the branching by reactions 3b and 4 does not yet lead to $pw > 1$. Nevertheless, and this is the sole important factor, either a material chain or an energy chain is involved, which is broken at the wall of the vessel. The reaction is accelerated not only by the water which is formed, but also by inert gases, including the noble gases, in the following order:

$$H_2O : A : N_2 : He = 5 : 4 : 3 : 1.$$

This gradation can be understood if it is assumed that the effect is due to lengthening of the chain by resistance to diffusion. The same rôle must, of course, be assigned to the reactants themselves. Although this cannot be directly proved, it is nevertheless possible to put forward mechanisms that satisfy the observed kinetics, when hydrogen is given the efficiency of helium and oxygen that of argon in retarding the diffusion.

Semenoff [75] has calculated the dependence of the chain length on the addition of foreign gases in this reaction, on the assumption of elastic collisions, and obtains results which approximately reproduce the observed velocities. The influence of a wide range of foreign gases upon the lower pressure limit of phosphorus oxidation has been studied by Melville and Ludlam,[75a] who account for their results on the basis of the coefficients of diffusion.

Finally, there is another way in which a chain can be lengthened by added gases. If the gas is adsorbed at the vessel wall it may poison the inhibiting

[73] C. H. Hinshelwood and W. H. Thompson, *Proc. Roy. Soc.*, A **118**, 170 (1928).
[74] C. H. Gibson and C. N. Hinshelwood, *Proc. Roy. Soc.*, A **119**, 591 (1928).
[75] N. Semenoff, *Z. physik. Chem.*, B **2**, 169 (1929).
[75a] H. Melville and E. Ludlam, *Proc. Roy. Soc.*, A **132**, 108 (1931).

recombination reaction. Thus, all reactions of atomic hydrogen are accelerated by water vapor (Wood, Bonhoeffer [76]), not directly, however, but because the reaction

$$H + H + \text{wall} = H_2 + \text{wall},$$

does not take place on moist walls. A similar explanation was suggested by Bodenstein and co-workers for the water catalysis of the formation of phosgene at moderate temperatures in light, while Norrish [77] suggests the same explanation in the case of the bromination of ethylene.

2. Negative Catalysis of Chain Reactions

We saw (p. 33) that true negative catalysis is impossible in simple non-chain reactions because, at equilibrium, a deactivation by the catalyst must always be accompanied by a corresponding activation. In chain reactions, however, the intermediate substance is not in equilibrium, but only in a stationary-state concentration, determined by the inter-relationships of the individual reactions. The equilibrium restriction therefore does not apply. Consequently, when an added substance reacts specifically with an intermediate or (in energy chains) specifically deactivates it, the occurrence of all the subsequent chain links is prevented and negative catalysis is observed. Negative catalysis is, therefore, an entirely special characteristic of chain reactions, as we shall see later in the case of solutions.

However, before discussing negative catalysis produced by direct reaction of the catalyst with intermediate substances, there is another important mechanism of negative chain catalysis to be mentioned, in which chains are shortened by positive catalysis of a chain breaking reaction.

Negative Catalysis of Chains by Positive Catalysis of Triple Collisions: The chain breaking reaction is a simple elementary reaction which forms stable end products, or reproduces the starting material, from unstable intermediate products, and is therefore exothermic. It is very frequently a recombination of free atoms if such are intermediates in the chain, as, for instance, bromine atoms in the formation of hydrogen bromide.

There are special limitations governing atom addition reactions such as:

$$Br + Br = Br_2,$$

which are particularly subject to the influence of catalysts. It has been

[76] R. W. Wood, *Phil. Mag.*, (6) **42**, 729 (1921); **44**, 538 (1922); *Proc. Roy. Soc.*, A **797**, 455 (1921); **102**, 1 (1922);
K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

[77] R. G. Norrish, *J. Chem. Soc.*, **123**, 1006 (1928).

shown theoretically, and proved by experiment, that these reactions do not occur in accordance with the bimolecular scheme given above, but only take place as termolecular reactions in triple collisions when a third molecule is present simultaneously, as, for example:

$$Br + Br + N_2 = Br_2 + N_2.$$

This was already foreseen by Herzfeld [78] on the basis of classical theory. At equilibrium, the rate of formation of bromine molecules is equal to the rate of decomposition. If a molecule is assumed to be formed whenever two atoms collide, the constant for the decomposition of bromine molecules, derived from the known position of equilibrium and the gas kinetic collision number is of such a high order that the mean life period of the molecule would be of the order of 10^{-13} sec., which is about equal to the collision period. All molecules formed in this way must, therefore, at once decompose again. This is because of the increased energy content due to the heat of formation, and we should expect the molecule to become stable only when it is in a position to give up this energy to a third body within the 10^{-13} sec. Conversely, the decomposition of bromine molecules is not a unimolecular but a bimolecular process.

The same result is obtained from quantum theory.[79] On purely mechanical grounds, the heat of reaction arising in a two atom collision cannot be converted into kinetic energy by an increase in the translational velocity of the molecule, since the velocity of the center of gravity must remain constant, as the whole system cannot accelerate itself. The same is true of the rotational motion. On the other hand, quantum theory forbids the distribution of the heat of reaction in the internal vibrations or electronic excitation of the molecule. Energy stored in these forms is quantized and, in the case of simple molecules with sharp quantum states, it is very improbable that there is an energy level exactly corresponding to the requirements. A stable molecule, therefore, cannot be formed in a two atom collision. The heat of reaction has to be taken up in relative translational motion of the atoms. In other words, the " quasi molecule " immediately decomposes again. If a third body is present in the collision, however, the difficulty disappears completely, since kinetic energy can now be transferred to this in any desired amount, so that the total heat of reaction goes into the velocity of the third body relative to the bromine molecule.

Two examples will be sufficient to demonstrate that these conclusions are in agreement with the facts. According to measurements of Bonhoeffer

[78] K. F. Herzfeld, *Z. physik. Chem.*, **8**, 132 (1922).

[79] M. Born and J. Franck, *Z. Physik.*, **31**, 411 (1925).

and Kaminsky,[80] the intensity of the afterglow of active nitrogen, due to the recombination of nitrogen atoms is proportional to $[N]^2 \cdot [N_2]$ (see also Kneser[81]). Again, it has also been shown by Bonhoeffer[82] and Senftleben and Riechemeyer[83] that the recombination of atomic hydrogen is a termolecular reaction.

As we have already remarked, the significance of this kind of catalysis for chain reactions (see also p. 29) lies in the fact that chains with atom intermediates are generally inhibited by added gases or by increase of pressure. This is very clearly illustrated in the formation of hydrogen bromide studied by Jost and Jung[72] (see also p. 54).

The reaction is assumed to take place in accordance with the following scheme:

1. $Br_2 = Br + Br$,
2. $Br + H_2 = HBr + H$,
3. $H + Br_2 = HBr + Br$ and so on as in 2,
4. $H + HBr = H_2 + Br$ (inhibition)
6. $Br + Br = Br'_2$ (quasi molecule),
8. $Br'_2 = Br + Br$ (immediately),
9. $Br'_2 + X = Br_2$

Reactions 6 and 9 together form the triple collision that alone breaks the chain. This scheme gives the velocity equation:

$$\frac{dx}{dt} = 2k_2 \sqrt{\frac{k_8}{k_6 k_9 p}} \frac{[H_2]\sqrt{I_0}}{1 + \frac{k_1[HBr]}{k_3[Br_2]}}$$

which corresponds to the observations of Bodenstein. I_0 is the intensity of the absorbed light, p is $\sum [X]$. The inhibition due to triple collisions is measured by the dependence on the total pressure. This appears in the expression in the inverse proportionality of k and $\sqrt{p}$, where k is given by $2k_2\sqrt{\frac{k_8}{k_6 k_9}}$. When the importance of the atom recombination in the gas phase diminishes in relation to that on the wall, that is, under conditions of greater light intensity, which gives higher atom concentration, in narrow vessels and at lower pressures, the influence of triple collisions disappears

[80] K. F. Bonhoeffer and G. Kaminsky, *Z. physik. Chem.*, **127**, 385 (1929).
[81] H. O. Kneser, *Erg. exakt. Naturwiss.*, **8**, 240 (1929).
[82] K. F. Bonhoeffer, *Erg. exakt. Naturwiss.*, **6**, 215 (1927).
[83] H. Senftleben and O. Riechemeyer, *Physik. Z.*, **30**, 745 (1929); *Naturwiss.*, **18**, 645 (1930).

and gives way to an acceleration by inhibition of diffusion, as we saw on p. 54.

Negative Catalysis Due to Chain-Breaking: The most frequently occurring and most important form of negative catalysis is, however, that in which the mean length of a reaction chain is diminished through a new reaction between the inhibitor and an intermediate, which breaks the chains. In agreement with our previous conclusions, Christiansen [84] has shown that this sort of inhibition is not possible in simple reactions, because, under stationary conditions, the influence of an added substance m, upon the velocity v, must diminish with decreasing m, thus:

$$\operatorname{Lim}_{m \to 0} \frac{dv}{dm} = 0$$

The appearance of negative catalysis in a thermal reaction therefore implies that it is composed of separate reactions in such a way that m, referred to the amount of intermediate, need no longer be considered small.

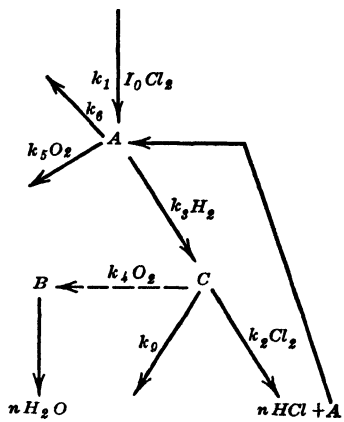


FIG. 4. Diagram of Reactions in Hydrogen-Chlorine-Oxygen Mixtures (Cremer).

Evidence of this conception has mainly to be obtained from reactions of known chain character, and whose mean chain length is amenable to investigation, that is, photochemical reactions or reactions in which the initial step can be introduced in some other measurable way. The most important example of this kind is the inhibition of the hydrogen-chlorine reaction by oxygen studied by Chapman and MacMahon,[85] by Bodenstein and Dux,[86] and by Cremer.[67] According to Cremer, all the results dealing with the formation of hydrogen chloride and the accompanying formation of water can be represented in the diagrammatic scheme given in Figure 4, which is here reproduced in the form applicable to the more recent developments of the atom chain theory of the reaction, which aside from side reactions and their velocities has yielded the indicated sequence of reaction intermediates. The arrows refer to the individual steps in the chain, and the symbols A, B, C, to intermediate compounds whose chemical individualities remain for the present unspecified.

[84] J. A. Christiansen, *Trans. Faraday Soc.*, **24**, 596 (1928).
[85] D. L. Chapman and P. MacMahon, *J. Chem. Soc.*, **95**, 959 (1909).
[86] M. Bodenstein and W. Dux, *Z. physik. Chem.*, **85**, 297 (1913).

The scheme is widely supported by experimental results. It follows, by inspection, that, as long as reaction 5 (i.e., $Cl + O_2 \xrightarrow{k_5}$ Products) is the only process breaking the chain, the velocity of formation of HCl is, as is found at higher oxygen pressures, inversely proportional to the oxygen pressure. Under the same conditions, the velocity of the simultaneous formation of water is not only proportional, but even equal, to the intensity of the absorbed light, so that two molecules of water are formed per quantum. This can only mean that the inhibition occurs by the side reaction 4 and every chain ends with the formation of water. This, therefore, obeys the Einstein law. Under other conditions, such as lower oxygen pressure and moist vessel walls, the chain breaking reactions 9 or 6 have to be taken into account, and consequently, the quantum yield of the water production decreases, since all chains do not now end in this way.

This scheme can now be interpreted with concrete molecular and atomic species for A, B, C . . . , since the difficulties urged against the atom chain mechanism of Nernst have been disposed of and since reaction 1 of the following sequence has been spectroscopically verified. The diagram corresponds most probably to the following reaction sequence:

1. $Cl_2 + h\nu = 2Cl$
3. $Cl + H_2 = HCl + H$
2. $H + Cl_2 = HCl + Cl$ and so on as in 3.
4. $H + O_2 + M = HO_2 + M$ (Triple Collision)
5. $Cl + O_2 + M = ClO_2 + M$ (Triple Collision)
6. $Cl \xrightarrow{Wall} \frac{1}{2}Cl_2$
9. $H + H + M = H_2 + M$ (Triple Collision)

Hence, in the diagram, A represents a chlorine atom, C a hydrogen atom, B the radical HO_2.

Bodenstein and Schenck[86a] have studied more closely the way in which the HO_2 radical is converted to water, by measuring the quantum yield of water formation with different gas ratios. They came to the conclusion, based on several lines of evidence, that reaction 5 does not finally lead to water formation, and that reaction 4, the main chain-breaker according to Cremer, leads to water formation by several paths indicated in the following:

[86a] M. Bodenstein and P. W. Schenck, *Z. physik. Chem.*, B **20**, 420 (1933).

First Path	Second Path
$HO_2 + H_2 = H_2O + OH.$	$HO_2 + Cl_2 = HCl + ClO_2$
$OH + H = H_2 + O$	$ClO_2 + H = HCl + O_2$
or	
$OH + Cl = HCl + O$	$ClO_2 + Cl = Cl_2 + O_2$
$O + 2HCl = H_2O + Cl_2$	

Third Path

$$HO_2 + HCl = H_2O + ClO$$
$$ClO + H = HCl + O$$
$$ClO + Cl = Cl_2 + O$$
$$O + 2HCl = H_2O + Cl_2$$

Kornfeld [86b] modifies the first path in the reactions of Bodenstein and Schenck to include the production of hydrogen peroxide by the mechanism of Taylor and Marshall. The sequence of reactions becomes:

1. $HO_2 + H_2 = H_2O_2 + H$
2a. $H_2O_2 + H = H_2O + OH$
2b. $H_2O_2 + Cl = H_2O + ClO$
2c. $OH + Cl = HCl + O$
2d. $ClO + Cl = Cl_2 + O$
3. $O + 2HCl = H_2O + Cl_2.$

In this example, a direct proof has been obtained that negative catalysis is due to the breaking of chains by a side reaction. We shall see later (p. 171) that entirely analogous evidence can be obtained for the inhibition of autoxidation in solution.

The inhibition by bromine of the hydrogen-chlorine or methane-chlorine reactions induced by the alkali metals is a clear case of the same type, according to Polanyi [87] and Polanyi and Bogdandy.[88] A measured number of chains can be originated by the vaporization of alkali metals instead of by irradiation with visible light, since every sodium atom " induces " a chain thus:

1. $Na + Cl_2 = NaCl + Cl.$

[86b] G. Kornfeld, *Z. physik. Chem.*, B **35**, 236 (1937).
[87] M. Polanyi, *Z. Elektrochem.*, **33**, 554 (1927).
[88] M. Polanyi, St. v. Bogdandy and H. v. Hartel, *Trans. Faraday Soc.*, **24**, 606 (1928).

The chain is then assumed to proceed according to:

2. $Cl + H_2 = HCl + H$ or $Cl + CH_4 = HCl + CH_3$,
3. $H + Cl_2 = HCl + Cl$ or $CH_3 + Cl_2 = CH_3Cl + Cl$

and so on as in 2. The chains are broken owing to removal of Cl, H or CH_3 at the walls. If, however, bromine is present, the chain is broken in yet another way:

4. $H + Br_2 = HBr + Br$ or $CH_3 + Br_2 = CH_3Br + Br$,
5. $Br = \frac{1}{2}Br_2$ (wall).

The observed inhibition by bromine can be represented quantitatively when k_4/k_3 equals 0.13 for hydrogen atoms and 0.3 for methyl radicals.

The majority of cases of negative chain catalysis can be explained in this way. Riesenfeld and Wasmuth [34] suggest a similar explanation of the inhibition of the first order decomposition of ozone by foreign gases (for the second order decomposition see p. 45) but it seems fairly certain (see Schumacher and Sprenger [35]) that a heterogeneous reaction governed by entirely different conditions is involved.

As already pointed out, a chain reaction, such as the hydrogen-chlorine combination, is often extremely sensitive to quite minute concentrations of an inhibitor. Bodenstein and Bernreuther [44a] showed that, in drying a hydrogen-chlorine mixture with phosphorus pentoxide, a volatile impurity was introduced into the gas mixture, which then obscured the 'drying effect' by its action in chain-breaking, and that, in addition, the use of gold chloride as the source of pure chlorine involves this chloride also as a chain-breaker. They could indeed show that the mere presence of mercury, gold or silicon introduces such an impurity. Bodenstein and Unger [88b] made it probable that reaction 6 of the preceding mechanism was caused by a volatile silicon chloride produced by the action of atomic chlorine on the glass walls. Bodenstein [88c] concludes that other chain reactions such as the hydrogen-oxygen reaction, phosgene formation, the formation of sulphuryl chloride, the dissociation of carbon dioxide, of which the reverse reaction is a chain reaction, and the formation of sulphur trioxide all suffer the same inhibition by phosphorus pentoxide.

Antiknocks: In the internal combustion engine, a mixture of combustible gas and air is drawn into the cylinder and then compressed by the return stroke of the piston. Towards the end of the compression stroke, the mixture should be fired in order to send the piston back again on the

[88b] M. Bodenstein and Unger, *Z. physik. Chem.*, B **11**, 268 (1930).
[88c] M. Bodenstein, *Z. physik. Chem.*, B **20**, 451 (1933); B **21**, 469 (1933).

working stroke by its expansion due to combustion. If, however, for any reason whatever, ignition occurs too early during the compression stroke, the explosion acts against the returning piston, giving a powerful shock or " knock " to the engine. With certain fuels, pre-ignition can be produced by the heat generated from adiabatic compression. Such fuels are described as " knocking."

It is an extraordinary phenomenon, having a wide technical application, that such fuels can be made " non-knocking " by the addition of very small amounts of certain substances. Lead tetra-ethyl and iron pentacarbonyl particularly, are known to be efficient in this direction. Also selenium diethyl, metallic vapors (K, Tl), aniline, phenol, and quinone act more or less strongly (Egerton [89]).

It is an obvious step to endeavor to trace the action of these additions to an elevation of the ignition temperature of a given mixture under the same conditions. If that were the case, higher compression could be used without the occurrence of pre-ignition. Berl, Heise and Winnacker [90] tested this point in a special apparatus and found, for example, the ignition points given in the accompanying Table V.

TABLE V

Fuel	Pure	1% $Fe(CO)_5$
n-Hexane.....	338° C	456° C
Benzine.....	415°	475°
Dapoline.....	300°	466°
	340°	460°
	415°	478°
Autobenzine.....	420°	472°

Thus far we have only been concerned with the actual description of phenomena. Let us now recall from p. 51 what is really meant by the " ignition " of a reaction mixture. It is the concentration or temperature, not at which reaction first begins, but at which the chain length rapidly attains the value of infinity. Expressed mathematically, pw in the expression

$$\frac{w}{1 - pw}$$

becomes equal to unity. Since w, the probability of further reaction of the

[89] A. Egerton, *Reunion Intern. de Chim. Phys.*, p. 489, Paris (1928).
[90] E. Berl, K. Heise, and K. Winnacker, *Z. physik. Chem.*, A **139**, 453 (1928).

chain, generally increases with increasing temperature, this happens above a certain temperature.

If this theory is also correct in the case of antiknocks, then these substances must also inhibit the pre-burning or slow, non-explosive oxidation of the same fuels below the ignition limit. Egerton, Berl, Heise, and Winnacker [89, 91, 91a] have also established that oxygenated products are formed considerably faster in a hexane-oxygen mixture alone, than with the addition of antiknocks.

The next point to be discussed is the form of the added material which is effective. First of all, from the fact that the order of efficiency is independent of whether the substance is added in the form of a liquid mixed with the fuel or whether it is introduced in the gaseous condition, Egerton [89] concludes that it is the vapor which is effective. Finally, it is probable that, in the case of organo-metallic compounds, the effect is due to the decomposition products and not to the molecule intact. For, according to Egerton,[89] certain metal vapors are effective, while according to Berl and Winnacker [92] a similar result can be obtained by admixture of colloidal metals with the fuel.

It might be concluded from these observations (Bodenstein [93]) that the effect is due simply to the greater surface of colloid particles, and therefore to the chains breaking at the " wall " formed in this way, as is so frequently observed (see p. 317). There are several indications, however, that the chemical nature of the wall has a decisive influence. Thus finely divided zinc oxide is without effect (Egerton [91]); likewise colloidal metallic oxides, which Berl and Winnacker admixed with the fuel, had no influence.

According to Berl and Winnacker,[94] analogous conditions prevail in the liquid phase, for example in the autoxidation of benzaldehyde. Antiknocks and dispersed metals are strongly inhibiting in this case also, but iron oxide, on the other hand, is not. In a recent communication, however, Pidgeon and Egerton [91] show that antiknocks which have been allowed to become oxidized by oxygen are more effective than the unoxidized material in inhibiting the slow oxidation of pentane, and that this inhibitory influence remains a property of the apparatus over a long series of experiments. They even consider the possibility of the effect being due to some surface change. Pidgeon and Egerton attribute the inefficacy of added metallic

[91] A. Egerton, *Trans. Faraday Soc.*, **24**, 697 (1928).

[91a] L. M. Pidgeon and A. C. Egerton, *J. Chem. Soc.*, 683 (1932).

[92] E. Berl and K. Winnacker, *Z. physik. Chem.*, A **145**, 161 (1929).

[93] M. Bodenstein, *Sitz.-ber preuss. Akad. Wiss. Physik-math. Kl.* **29**, 3 (1928); *Z. Elektrochem.*, **35**, 535 (1929).

[94] E. Berl and K. Winnacker, *Z. Physik. Chem.*, A **148**, 261 (1930).

oxides (see Berl and Winnacker above) to their relatively low state of dispersion.

Since unstable peroxides have been known from the time of Engler, to be intermediate steps in autoxidation processes, it is reasonable to suppose that similar products occur in explosion reactions.

The mechanism of the explosive reaction is uncertain, but Egerton [91] has suggested the following chain mechanism:

$$1.\ O'_2 + A = AO'_2,$$
$$2.\ AO'_2 + A = AO + AO',$$
$$3.\ AO' + O_2 = AO + O'_2 \text{ and so on as in 1,}$$

in which A refers to the fuel. The chains may be broken either at the wall, since this dissipates the excitation energy:

$$4.\ \text{Wall} + AO'_2 = \text{wall } O + AO,$$

or at a metallic peroxide:

$$5.\ MeO_2 + AO'_2 = MeO + AO + O_2,$$

the energy of excitation being nullified by distribution among three molecules. According to Berl and Winnacker [94] the reaction:

$$5.\ MeO_2 + AO'_2 = Me + A + 2O_2,$$
$$Me + O_2 = MeO_2,$$

should also be possible. Such a regeneration of the metal or its peroxide would account for the fact that metallic compounds (Egerton [91]) are much more effective than pure organic antiknocks. The views developed here also correspond to those advanced by Moureu [95] (see also p. 171).

It seems very probable, on the other hand, that dehydrogenation processes play an important rôle in the combustion of hydrocarbons. Haber and Bonhoeffer [54] have shown that spectroscopic evidence and energy considerations support this view, while it is favored by Wieland [96] for chemical reasons. Lewis [97] has built it up into a dehydrogenation theory of explosion, in which H_2 is first of all split off and subsequently oxidized to H_2O or H_2O_2.

Berl endeavored to combine both views [90, 92] by supposing that the peroxide is formed from the dehydrogenated radical

$$R-CH_2\,CH_3 + \text{Heat} = R-\dot{C}\cdot CH_3 + 2H \text{ or } RCH_2CH- + 2H.$$

[95] C. Moureu and C. Dufraisse, *C.r. Acad. Sci. Paris.* **174**, 258 (1922); **176**, 624 (1923); Conseil de Chimie, Institut Intern. de Chimie Solvay, p. 524, Paris, 1925.

[96] H. Wieland, *Ber.*, **45**, 484 (1912).

[97] J. S. Lewis, *J. Chem. Soc.*, 1555 (1927).

Then, on the one hand, a kind of Haber OH-chain is set up, expressed at one time by the equation:

$$\begin{aligned} 2H \quad &+ O_2 = 2OH \\ OH \quad &+ H = H_2O \\ R' \cdot CH_3 &+ OH = R'CH_2 + H_2O \end{aligned}$$

On the other hand there also result peroxides

$$R-\dot{\underset{\cdot}{C}}-CH_3 + O_2 = R-C \cdot \begin{matrix} CH_3 \\ O-O \end{matrix}$$

$$R-CH_2-CH: + O_2 = R-CH_2 \cdot CH\begin{matrix} O \\ | \\ O \end{matrix}$$

and, at these peroxides, which propagate the peroxide chains, the inhibition occurs by reactions such as

$$R''O_2 + 2Pb = R'' + 2PbO.$$

or $$R''O_2 + PbO_2 = R''O + PbO + O_2.$$

Bodenstein [97a] regards the radical which results from the opening-up of a double bond and the activated form of the peroxide as the joint links of a single reaction chain.[97b] He finds this point of view to be in kinetic agreement with his own measurements on the oxidation of acetaldehyde, the measurements of Spence and Kistiakowsky [97c] on acetylene and with data for other organic vapors. The mechanism is thus formulated:

(1) $A \rightarrow A'$ (activation)

(2) $A' + O_2 = P'$ } chain

(4) $P' + A = P + A'$ and so on by (2) } chain

(3) $P' = A' + O_2$.

(4') $P' + K = P + K'$ (Inhibition by antiknock)

(5) $P' + O_2 = P + O_2$ (Chain breaking)

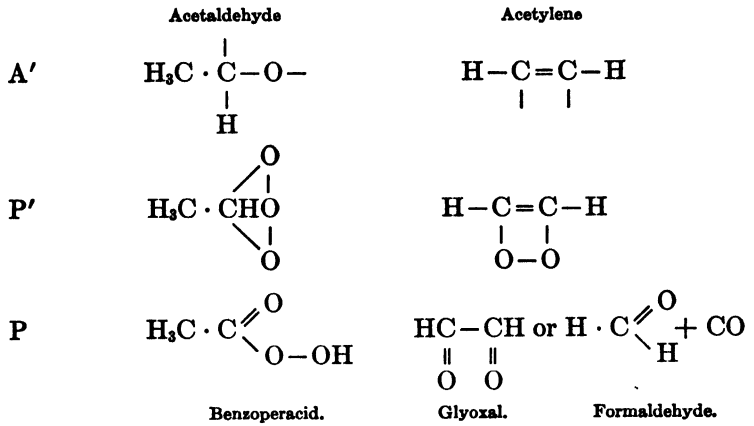
(6) $P' + \text{Wall} = P$ (Chain breaking)

The intermediates A' and P' and the final products P signify in the cases of acetaldehyde and acetylene the following compounds or radicals:

[97a] M. Bodenstein, *Sitz.-ber. Preuss. Akad.*, 1931, III; *Z. physik. Chem.*, B **12**, 151 1931).

[97b] See, however, W. H. Thatcher, E. W. Steacie and F. Howland, *Can. J. Res.*, **7**, 149 1932).

[97c] R. Spence and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **52**, 4837 (1930).



On the whole it is evident, therefore, that while the real nature of the chains is still not completely understood and leaves room for speculation, the concept of chain-breaking affords a very illuminating explanation of the inhibitory action, especially since it is certain that explosions involve chain reactions.

CHAPTER V

HOMOGENEOUS CATALYSIS IN SOLUTION. I

The Concept of Intermediate Steps

The homogeneous catalysis of gas reactions is, as we have already seen, a comparatively infrequent phenomenon, confined to specially favorable individual cases. Its occurrence is due not so much to some general requirement of chemical dynamics as to the nature of the catalyzed system whose specific affinities determine the appearance and efficiency of definite intermediate stages. In particular, there can now be no longer any doubt that uncatalyzed homogeneous gas reactions are not only imaginable, but actually are to be observed in considerable numbers.

The reactions of dissolved substances, on the other hand, present, even at first glance, an entirely different picture. Indeed, we should expect from the circumstance that the presence of the solvent has quite another influence on the velocity than an " inert " gas in gaseous reactions, that it will hardly be possible to separate such reactions from catalytic influences (disregarding for the moment two exceptions — the decomposition of nitrogen pentoxide and the isomerization of pinene (see p. 154)). In special cases, for example, the mutarotation of glucose and some of its derivatives, Lowry [98] has even shown that the change can be completely stopped in certain solvents by the careful removal of catalysts. One is almost inclined to postulate, therefore, that, in solution, catalyzed reactions are the rule and uncatalyzed processes the exception, at least as far as measurable velocities are concerned.

Actually, in complete contrast to gas reactions, the number of solution catalyses investigated in the last ten years alone is so vast, that not the remotest attempt can be made to discuss all of them, or even all of their types, in the following pages. We shall have to limit ourselves more particularly to the consideration of those cases which are of special significance with respect to the nature of catalysis.

This circumstance is certainly due in part to the nature of the reactions concerned. Gas reactions occur either between very simple and there-

[98] T. M. Lowry and E. M. Richards, *J. Chem. Soc.*, **127**, 1385 (1925); T. M. Lowry and J. I. Faulkner, *J. Chem. Soc.*, **127**, 2883 (1925).

fore very firmly bound molecules or, at high temperatures, involve very considerable activation energies. They represent, therefore, what Lowry [99] alludes to as " rather brutal " processes, and a catalyst taking part in such energy exchanges has to possess considerable selective affinities. Reactions in the field of liquid solutions, on the other hand, occurring at about room temperature, such as hydrolysis or enolization, for instance, are quite the opposite. They usually concern far subtler rearrangements of relatively complicated molecules and it is obvious that, in such processes, the velocity will be much more readily influenced by a third body.

On account of its polar nature, it is also to be expected that our commonest solvent, water, will have a particularly widespread catalytic influence, since it favors the production of ions which can exert electrostatic, deformative forces upon one another and on polar or polarizable molecules.

Intermediate Reaction in Solution: In the discussion of gaseous catalysis it has nearly always been possible to represent the reactions successfully as a series of separate bimolecular steps, that is, to resolve them into intermediate reactions. As far as the explicit form of the velocity equation is concerned, it does not matter whether the intermediate product arising through such intermediate reactions has a long life and can be isolated like ClO_3 in the catalysis of the ozone decomposition by chlorine, or whether, like COCl in the catalysis of the decomposition of phosgene by chlorine atoms, it is present only in extremely small stationary concentration. This only affects the constants which, by the introduction of approximations, lead to the kinetic equation in its final form.

As we shall shortly see, this final equation appears to be formally identical in the limiting cases of both possibilities. Furthermore, for reasons already given, the number of theoretically possible intermediate substances is greater in solution, and hence the question of the life period of the intermediate substance is of much greater interest in this case.

The Friedel-Kraffts reaction, for instance, can be successfully resolved into a reaction series of preparable intermediate substances or addition compounds:

$$RCOCl + AlCl_3 \rightleftarrows RCOCl \cdot AlCl_3,$$
$$RCOCl \cdot AlCl_3 + C_6H_6 \rightleftarrows RCOC_6H_5 \cdot AlCl_3 + HCl,$$
$$RCOC_6H_5 \cdot AlCl_3 \rightleftarrows RCOC_6H_5 + AlCl_3.$$

According to Boeseken,[100] however, this is no proof that the above formulation affords an adequate representation of the mechanism, since it

[99] T. M. Lowry, *Trans. Faraday Soc.*, **24**, 545 (1928).
[100] J. Boeseken, *Trans. Faraday Soc.*, **24**, 611 (1928).

is possible to find substrates like chloroform, ethylene, etc., which do not form such molecular compounds and can still be catalyzed, and others like phosphorus oxychloride, which gives crystalline compounds without undergoing the reaction. Boeseken [101] concludes from this as well as from the possibility of photosensitizing the reaction that the fundamental process is not the formation of an intermediate compound, but simply the displacement of the field within the molecule, a so-called "dislocation." This dislocation must take place at the instant of collision with the catalyst, or at the instant of separation, leaving the substrate in a reactive, "opened," condition. The life period of this open state is then of the order of magnitude of the collision period, 10^{-12} sec.

The obvious difficulty that a reaction between two substrates A and C would require the assumption of a triple collision can be overcome, according to Lowry [99] if the real substrate is considered to be a compound AC, already existing in equilibrium. The existence of ester-water compounds in the hydrolysis of esters, for example, seems probable from depression measurements of Kendall and Harrison.[102]

The modification put forward by Lowry would lead to the mechanism (K refers to the catalyst):

Without a catalyst	With a catalyst
$A + C = AC$,	$A + C = AC$,
$AC = AC'$ extremely seldom	$AC + K = AC' + K$ (faster, but velocity determining)
$AC' = B$ very rapid,	$AC' = B$ very rapid

Boeseken himself nevertheless seems to incline more to the view of triple collisions, since he says, "In a bimolecular physical catalysis both the molecules, together with the catalyst, attain the intermediate stage at the same moment . . . " That would mean:

Without a catalyst	With a catalyst
$A + C = AC'$ extremely seldom,	$A + C + K = ACK'$ (faster, but velocity determining)
$AC' = B$ very rapid	$ACK' = B + K$ very rapid

He considers that the acceleration is due, not to a diminution in the energy of activation, but rather to an increase in the entropy change with activa-

[101] J. Boeseken, *Kon. Akad. Wetensch. Amsterd.*, **31**, 226 (1923).
[102] J. Kendall and L. Harrison, *Trans. Faraday Soc.*, **24**, 588 (1928).

tion, in the sense of Scheffer and Kohnstamm,[103] i.e., to an increase in the " steric factor," the catalyst increasing the " sensitive range " of the molecule. Van Thiel [104] has actually established catalysis by sulphuric acid, in the coupling of acetic anhydride with diphenylamine with simultaneous doubling of the energy of activation. V. K. LaMer [104a] points out that quite generally, in solution, the reaction constants are able to compensate increases in activation energy by reason of the entropy change on activation apart entirely from any steric factor. As a consequence, accelerations with enhanced activation energies are not only possible but often found, as in the primary salt effect to be discussed later.

It is questionable, however, whether such effects suffice, generally, to compensate for the greater frequency, by several powers of ten, of the two body collisions by which the uncatalyzed reaction occurs. It is difficult, therefore, to avoid having to assign a greater life to the state of addition of at least two of the components. This does not cause any alteration in the form of the velocity equation, since both assumptions lead to the equation:

$$dx/dt = k[\mathrm{A}]\,[\mathrm{C}]\,[\mathrm{K}].$$

It seems to be possible in this way, to bring the theory of intermediate reactions into contact with the " dislocation " theory. Even with an intermediate compound, the action of the catalyst is to loosen the atom-bond which is necessary for reaction to proceed. Thus, Boesèken shows that the addition of the catalyst in the wrong position, perhaps of $AlCl_3$ to the nitro group of nitro-benzyl chloride, inhibits rather than promotes reaction. It is essential that the intermediate compound be so constituted that the substrate molecule is attacked in the right place, and furthermore, that it is not too stable. Ostwald [105] early called particular attention to the fact that the mere existence of an addition compound does not constitute proof of its rôle as an intermediate, it must also react rapidly, that is, it must have a certain degree of instability, at least in the environment concerned.

Kinetics of Intermediate Reactions: It is characteristic of the state of affairs appertaining to solutions, that the life period of the intermediate stages cannot be decided from the reaction kinetics which are almost entirely isothermal, heats of activation having scarcely been measured in solution catalysis. Skrabal [106] has given a general formulation to the special,

[103] F. E. L. Scheffer and P. Kohnstamm, *Proc. Amsterd. Akad.*, **13**, 789 (1922); **15**, 1109 (1913).

[104] E. v. Thiel, *Kon. Akad. Wetensch. Amsterd.*, **31**, 232 (1923).

[104a] V. K. LaMer and M. E. Kamner, *J. Am. Chem. Soc.*, **37**, 2662 (1935).

[105] W. Ostwald, *Physik. Z.*, **3**, 313 (1902).

[106] A. Skrabal, *Trans. Faraday Soc.*, **24**, 687 (1928).

but also most widespread, example of acid-base catalysis, which is the basis of so many reactions (esterification, saponification, inversion, mutarotation, enolization, many oxidations and reductions). Essentially, his method is not very different from the treatment already employed in the case of gas reactions by Herzfeld.[21]

The general scheme for a change A → B catalyzed by C will be:

$$1.\quad A + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z,$$

$$3.\quad Z \xrightarrow[k_3]{} B + C,$$

where Z is the intermediate stage and can either be a compound AC, or an unstable collision complex of A and C with corresponding dislocation in A. This alternative is determined only by the relative values of the constants k_1, k_2 and k_3. Making the usual assumption that in the stationary state, Z disappears as rapidly as it is formed (or the probability of its disappearance is unity; compare p. 11), the total velocity becomes:

$$\frac{d[B]}{dt} = \frac{k_3 k_1 [A]\,[C]}{k_2 + k_3} = k[A]\,[C].$$

In all cases then, what is measured is only the proportionality to the concentration of the catalyst and substrate, without the stability of the intermediate substance, or the values of the individual constants being determinable. With regard to the latter, we have the following possible limiting cases.

The Arrhenius Intermediate: When $k_2 \gg k_3$, it is evident that the equilibrium between A, C and AC, whose constant K_1 is given by:

$$K_1 = \frac{k_1}{k_2},$$

is not essentially disturbed by the reaction of a small fraction of Z (primary equilibrium). We, therefore, obtain:

$$\frac{d[B]}{dt} = k[A]\,[C] = k_3 K_1 [A]\,[C].$$

Here, the velocity determining process is the decomposition of Z. In this case Z is termed an "Arrhenius intermediate," because the energy rich molecules assumed in the derivation of the Arrhenius temperature function of velocity,[107] belong to this type (compare p. 25). We shall see that Euler's

[107] S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

theory (see p. 115) of interacting ions postulates an intermediate of this kind. Skrabal [106, 108] has remarked in connection with the latter, that the theory cannot be proved, because k_3 and K for the ions assumed in most substrates (sugars and esters), possess values which are too extreme to give trustworthy measurements. We shall see, later, that Bjerrum [109] assumes Arrhenius compounds of this catalyst-substrate type to explain the kinetics of the neutral salt effect.

The van't Hoff Intermediate. The other limiting case is obtained when $k_3 \gg k_2$, i.e., the intermediate product decomposes so slowly that it is used up in the reaction giving B, as quickly as it is formed. Its rate of formation according to reaction 1 determines the velocity and we obtain:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]\,[\mathrm{C}].$$

The term "van't Hoff intermediate" is applied to these substances, because it was by such means that van't Hoff was able to explain how, in many reactions, the velocity determining step is of lower order than the gross equation. A special conception of this type of intermediate forms the basis of the Brönsted explanation of the salt effect (see p. 137). Rice [110] also inclines to a similar view.

Investigations making use of the heavy hydrogen isotope, deuterium, have made possible a partial decision in this problem, as in many other similar cases. Whereas all reactions involving molecular deuterium or deuterium oxide take place more slowly than those with the lighter isotope owing to the heavier mass and the larger activation energy, due to differences in zero point energy, the same being true also of mutarotation by D_3O^+ in respect to that with H_3O^+ ion, the inversion of cane sugar, on the contrary, is more strongly catalyzed by the heavy hydrogen ion than by the lighter ion.[110a] This can be interpreted on the assumption that an Arrhenius-intermediate is formed, whose K_1, the equilibrium constant is greater in the case of the heavy hydrogen ion, so that the decrease in k_3 is thus compensated. Similar conclusions have been reached by Salzer and Bonhoeffer [110b] for enzyme reactions.

The important result that mutarotation is not produced by an acid or basic solvent medium alone but only when they are combined with one

[108] A. Skrabal, *Z. Electrochem.*, **33**, 322 (1927).
[109] N. Bjerrum, *Z. physik. Chem.*, **108**, 82 (1924).
[110] F. O. Rice and J. J. Sullivan, *Trans. Faraday Soc.*, **24**, 678 (1928).
[110a] E. A. Moelwyn Hughes, *Z. physik. Chem.*, B **26**, 272 (1934), B **26**, 281 (1934); E. A. Moelwyn Hughes, R. Klar and K. F. Bonhoeffer, *ibid.*, A **169**, 113 (1934).
[110b] F. Salzer and K. F. Bonhoeffer, *Z. physik. Chem.*, A **175**, 304 (1936).

another or with an amphoteric substance, was established by Lowry.[111] This requires the consideration, from the same point of view, of the effect of *two* catalysts in one reaction. The reaction scheme is as follows, C being the one catalyst, M the other:

$$A + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z_1,$$

$$Z_1 + M \underset{k_4}{\overset{k_3}{\rightleftarrows}} Z_2 + C,$$

$$Z_2 \xrightarrow{k_5} B + M,$$

from which we obtain, in the same manner as above, the general equation:

$$\frac{d[B]}{dt} = \frac{k_1 k_3 k_5 [A]\,[C]\,[M]}{k_3 k_5 [M] + k_2 k_4 [C] + k_2 k_5 + [M]\,[C]\,k_3 k_4}$$

Here also, the experimental equation is:

$$\frac{d[B]}{dt} = k[A]\,[C],$$

with which only the following cases are reconcilable:

1. *Z_1 is of the van't Hoff type, Z_2 is likewise a van't Hoff intermediate,* i.e., $k_3[M] \gg k_2$ and $k_5 \gg k_4[C]$, giving:

$$\frac{d[B]}{dt} = k_1[A]\,[C].$$

2. *Z_1 is of the Arrhenius type, Z_2 is a van't Hoff intermediate,* i.e., $k_2 \gg k_3[M]$ and $k_5 \gg k_4[C]$, giving

$$\frac{d[B]}{dt} = k_3 \cdot \frac{k_1}{k_2}[A]\,[C]\,[M] = k_3 K_1 [A]\,[C]\,[M],$$

and since the second catalyst M is always in constant concentration in the excess of water present, the factor [M] can be omitted.

3. *Z_1 is an Arrhenius intermediate, Z_2 is similarly of the Arrhenius type,* i.e., $k_2 \gg k_3[M]$ and $k_4[C] \gg k_5$, and we find

$$\frac{d[B]}{dt} = k_5 \cdot \frac{k_1 k_3}{k_2 k_4}[A]\,[M] = k_5 K_1 K_2 [A]\,[M].$$

[111] T. M. Lowry, *J. Chem. Soc.*, **129**, 2554 (1927).

The same holds for [M] as in case 2. It is evident, nevertheless, that case 3 is not in agreement with experiment as it would require independence of catalyst concentration, [C], and therefore of the concentration of acid or base. It can easily be shown that case 4, where Z_1 would be a van't Hoff and Z_2 an Arrhenius intermediate, likewise is not in accord with the results. In each case, therefore, it may be said that Z_2 must be a van't Hoff intermediate; with respect to Z_1, however, the compound of the substrate with what is in the ordinary sense the " proper " catalyst, the question still remains open. We shall first of all attempt to arrive at a decision on this point by a discussion of the fundamental problems.

We have supposed hitherto, that the concentration of the intermediate substance is vanishingly small (owing to its great instability) compared with that of the substrate and catalysts. However, this is not always the case. It is known that catalysis can still be effected by intermediates of the Arrhenius type (with the restriction given on p. 72), even when so stable as to exist in concentration commensurable with the concentrations of catalysts and substrate. In these circumstances, their existence demands the withdrawal of a considerable portion of the other reactants and the hypothesis hitherto used in our calculations no longer holds good. This case is particularly frequent in enzyme catalysis where it was first given general treatment, and the problem will again be taken up in this connection (p. 335). The equations relating to purely homogeneous catalysis have been deduced by Spitalsky.[112] He also found that the chromate-chromic acid catalysis of the decomposition of hydrogen peroxide [113] can be satisfactorily explained on this basis.

In this case we have the reaction:

$$A + C \rightleftarrows Z,$$

with the equilibrium constant:

$$K = \frac{[Z]}{[A]\,[C-Z]},$$

and the velocity, proportional to the Arrhenius intermediate, becomes:

$$\frac{d[B]}{dt} = \frac{k_3 K[C]\,[A]}{1 + K[A]}.$$

It is important to observe that the reaction accordingly does not need to have a whole number " order " towards the substrate, but rather can vary

[112] E. Spitalsky, *Z. physik. Chem.*, **122**, 257 (1926).
[113] E. Spitalsky and N. Koboseff, *Z. physik. Chem.*, **127**, 129 (1927).

between zero order (catalyst all combined as Z) and first order (Skrabal's limiting case, see above) according to the magnitude of K. If n molecules of A are combined in the intermediate, [A] in the above expression is raised to the nth power. Two especially important examples will be taken from the numerous conceivable cases that Spitalsky systematically discussed.

We shall consider, first of all, the case in which two catalysts are effective side by side. The second catalyst may influence only the k appertaining to the velocity determining decomposition of the intermediate compound of the first catalyst; its concentration then enters as a factor in the velocity expression. This case is important with regard to the influence of acidity in various reactions, particularly again in enzyme reactions. When, however, both catalysts form a common intermediate product that subsequently decomposes, the situation becomes more difficult. We have then to write:

$$\begin{aligned} &A + C_1 \rightleftarrows Z_1, \\ &A + C_2 \rightleftarrows Z_2, \\ &Z_1 + C_2 \rightleftarrows Z_2 + C_1 \rightleftarrows Z. \end{aligned}$$

If the substance Z, which contains both catalysts, now decomposes to give the end product B, we obtain

$$\frac{d[B]}{dt} = \frac{kK[C_1]\,[C_2]\,[A]}{1 + K[A]\,[C_1 + C_2]},$$

and when Z_1 and Z_2 also furnish B, the catalysts C_1 and C_2 are separately effective:

$$\frac{d[B]}{dt} = \frac{k_1K_1[C_1]\,[A]}{1 + K_1[A]} + \frac{k_2K_2[C_2]\,[A]}{1 + K_2[A]} + \frac{kK[C_1]\,[C_2]\,[A]}{1 + K[A]\,[C_1 + C_2]}.$$

Since the sum of the first two terms in this expression would correspond to the additive effect of the independent catalysts, the introduction of the third, interaction term, leads to the important phenomenon of catalytic *promotion*, in which *additivity is exceeded.* Cases of this kind are to be found in the combined action of copper-iron in a number of oxidation-reduction reactions. This important class of phenomena will be discussed separately, but it is already evident that, in principle, these phenomena are readily comprehensible.

Spitalsky's chief object is to point out that integral orders of reaction should not be specially sought after or overemphasized, since they are not always to be expected on theoretical grounds and it is often doubtful to which general equation they belong as limiting case.

The following scheme, which we are now going to consider, is very instructive in this connection:

$$A + C \rightleftarrows Z_1 \rightarrow B + C,$$
$$2A + C \rightleftarrows Z_2 \rightarrow 2B + C.$$

The appropriate velocity equation:

$$\frac{d[B]}{dt} = \frac{[C]\,[k_1K_1[A] + k_2K_2[A]^2]}{1 + K_1[A] + K_2[A]^2},$$

plotted as a function of the substrate concentration, assumes the forms shown in Fig. 5, according to the relative values of the velocity and equilibrium constants. It is interesting to note that because the catalyst is involved in both equilibria simultaneously, it is actually possible for maxima to appear. In enzyme catalysis such maxima are found quite frequently as a consequence of the formation of different Z-bodies.[113a]

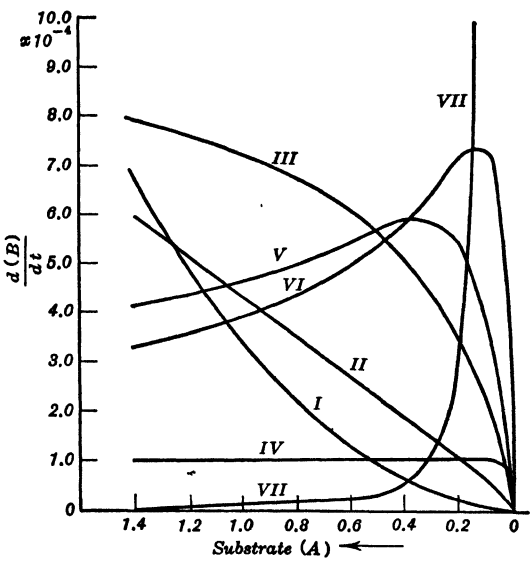


FIG. 5. Types of Dependence of Velocity upon the Substrate in a Reaction Involving Two Intermediate Compounds (Spitalsky).

Additional maxima and minima are obtained with more intermediates. Spitalsky and Koboseff [113] kinetically investigated a case of this type, the catalysis of the decomposition of hydrogen peroxide by chromates and chromic acid, and were able, at the same time, to follow the concentration of the intermediates by conductivity measurements. The theory was confirmed and even the position of certain intermediate equilibria determined.

It appears from these kinetic considerations, that the theory of intermediate compounds actually yields the types of velocity equation observed

[113a] See later sections of this book as well as Haldane-Stern, General Chemistry of Enzymes; G.-M. Schwab, E. Bamann and P. Laeverenz, *Hoppe Seylers' Z. physiolog. Chem.*, **215**, 121 (1933).

in catalysis in solution, and therefore attains a considerable degree of probability, especially as we have seen that it includes the possibility of dislocation. On the other hand, however, definite deductions regarding the exact form of the mechanism and the relations of its steps cannot usually be made from the observed kinetics, especially when the observations represent an ambiguous limiting case of general tendencies, as we find with the most effective catalysts (acid-base catalysis). It is only in the comparatively rare cases, where at least the intermediate steps can be observed separately, or in the cases in which other physical observations permit conclusions about a postulated step in the total process, as for example, when heavy water has taken part in the reaction, that complete clarification of the mechanism is possible. On the other hand, we saw that the theory offers some explanation of certain characteristics of catalysis, such as its *selectivity* and the *promotor effect.* This will appear even more clearly as we proceed. In many cases, moreover, kinetic measurements form some sort of basis for discussion as to which of the many possible molecular species represents the true catalyst. This discussion will take up a large part of our attention.

Catalyses Deducible from Intermediate Reactions: We shall discuss first of all, some cases in which it has actually been possible to represent or predict quantitatively, the amount of catalytic acceleration, by combination of separate reactions of known, measurable velocity, fulfilling Ostwald's postulate [105] that: " The reaction velocities in question must actually be measured, and until that is done, one can only speak of a conjecture, not of a solution." It is probably clear from the foregoing, that only a fortunate coincidence of suitable values of the velocities involved makes this fulfillment of the postulate possible. Such cases are therefore very rare.

1. The Iodide Ion Catalysis of the Decomposition of Hydrogen Peroxide: The first practical example of this kind was the decomposition of hydrogen peroxide catalyzed by iodide ions. This process was first accurately investigated by Bredig and Walton.[114] They agitated the neutral reaction mixture and measured the amount of oxygen developed. Scarcely any iodide ion was oxidized in neutral solution and therefore 100% of the hydrogen peroxide disappearing formed O_2. According to these measurements:

$$\frac{d[O_2]}{dt} = k[H_2O_2]\,[I'],$$

which gives identical values of k for KI and NaI. The same value was also obtained for NH_4I, after correcting for the incomplete dissociation of this

[114] G. Bredig and J. H. Walton, *Z. Elektrochem.*, **9**, 114 (1903); J. H. Walton, *Z. physik. Chem.*, **47**, 185 (1904).

salt from the conductivity. In the case of CdI_2, a deviation of about 35% remains after such a correction, which is evidently to be explained by a stepwise dissociation and complex formation. It is important that all additions which remove iodide ions by complex formation, such as molecular iodine and mercuric iodide, for example, act as inhibitors. The total salt concentration has no effect (see p. 140). In all cases, therefore, the velocity is proportional to the concentration of iodide ions.

While Bredig and Walton chose to explain their results by a transference of the oxidizing effect from one molecule of H_2O_2 to a second by the iodide ion through IO′, Abel [115] succeeded in connecting the reaction with known processes by another mechanism, and, in this way, he could calculate the velocity.

In the first place, Abel considered another reaction. In acid solution, the following processes occur simultaneously:

$$\text{I.}\quad H_2O_2 + I_2 = 2H^{\cdot} + 2I' + O_2 (H_2O_2 \text{ reduces } I_2),$$

$$\text{II.}\quad H_2O_2 + 2H^{\cdot} + 2I' = 2H_2O + I_2 (H_2O_2 \text{ oxidizes } 2I').$$

Summing, we obtain:

$$2H_2O_2 = 2H_2O + O_2,$$

representing the simple decomposition. As soon as both reactions proceed with equal rapidity, the iodine and iodide ion concentrations become stationary and we have a " pure catalysis," which Abel designated " iodine-iodide ion catalysis."

Reaction (I) is retarded by H ions and accelerated by I_2. Hence, an increase in (II) causes (I) to become faster, until at a definite ratio, I_2/I', the velocities are equal and " pure catalysis " is attained. Since the rates of both reactions are proportional to $[H_2O_2]$, their ratio is independent of the latter, but, on the other hand, is dependent on the hydrogen ion concentration.

It is now possible to calculate the ratio of the concentrations of I_2 and I' necessary for pure catalysis. The velocity of (II) has been determined by Noyes and Scott,[116] and that of (I) can be measured in moderate hydrogen ion concentration, buffered, because, otherwise, $H^{\cdot}$ from (II) would soon retard strongly. These measurements give the values of I_2/I' requisite for pure catalysis at every hydrogen ion concentration. If the velocity of the pure catalysis is now measured, it is found to be the same for all con-

[115] E. Abel, *Z. Elektrochem.*, **14**, 598 (1908). See also W. C. Bray, *Chem. Reviews*, **10**, 172 (1932).

[116] A. A. Noyes and W. O. Scott, *Z. physik. Chem.*, **18**, 118 (1895); **19**, 601 (1896).

centrations of hydrogen ion. It must, of course, be equal to twice the velocity of (I), since O_2 is measured in mols and H_2O_2 in equivalents, and similarly to twice the velocity of (II), since the velocities of (I) and (II) are equal. According to Noyes and Scott, the velocity of the latter is $0.667[I'][H_2O_2]$, whence the velocity of the catalysis must be:

$$\frac{d[O_2]}{dt} = 1.33[I'][H_2O_2],$$

independent of hydrogen ion concentration. This was afterwards confirmed in all cases even to the numerical value.

This calculation of the iodine-iodide ion catalysis may be extended automatically to Bredig and Walton's " iodide ion " catalysis. In neutral solution, even without the introduction of iodine, a small amount of the latter will, of course, be produced, sufficient, because of the high velocity of (I), to lead to equal velocities and pure catalysis. Consequently, this will be established almost at once, and, in fact, the neutral solution is always colored a pale yellow. The constant of the catalysis, therefore, should be the same as in the previous case, namely, 1.33. Bredig and Walton had actually measured values deviating little from 1.4. Thus, the process may be quantitatively traced to alternate oxidation and reduction of iodide ions or iodine by hydrogen peroxide, and can be calculated from this velocity. Newer measurements by Liebhafsky and his co-workers [116a] confirm the results of Abel in all essentials.

2. The Iodide Ion Catalysis of the Hydrogen Peroxide-Thiosulphate Reaction: Previous to his explanation of the earlier experiments of Bredig, Abel [18] investigated another reaction which he succeeded in calculating quantitatively. The uncatalyzed process:

$$H_2O_2 + 2S_2O_3'' + 2H^{\cdot} = 2H_2O + S_4O_6'',$$

proceeds according to the equation:

$$\frac{dx}{dt} = 1.53(a - x)(b - x),$$

where a is the initial concentration of the peroxide, b that of the thiosulphate, and x is the amount changed. The reaction is accelerated by iodide ions.

Abel suggests that the primary and velocity determining process in the catalysis is the Noyes-Scott reaction:[116]

$$H_2O_2 + I' = H_2O + IO',$$

[116a] H. A. Liebhafsky, *J. Am. Chem. Soc.*, **54**, 1792, 3499 (1932); **55**, 3977 (1933).

giving IO′ as a van't Hoff intermediate, followed immeasurably rapidly either by:

$$IO' + I' + 2H^{\cdot} = I_2 + H_2O \text{ (as in the previous example),}$$
$$I_2 + 2S_2O_3'' = S_4O_6'' + 2I',$$

or, what amounts to the same thing, by:

$$IO' + 2S_2O_3'' + 2H^{\cdot} = S_4O_6'' + I' + H_2O.$$

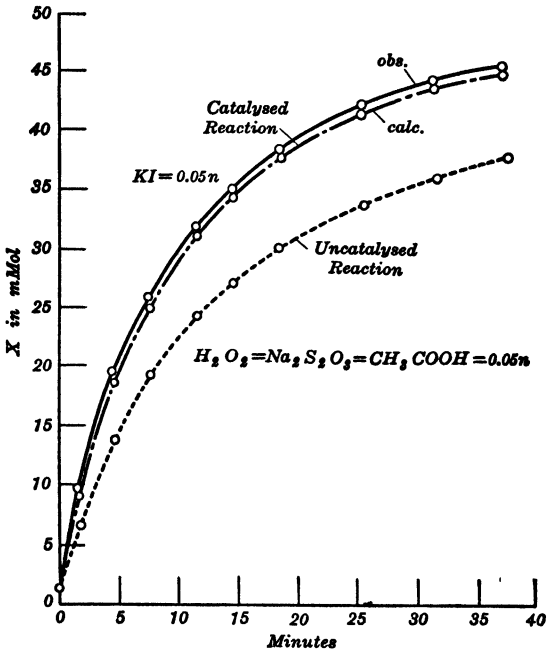


FIG. 6. Iodide Ion Catalysis in the Reaction between Hydrogen Peroxide and Thiosulphate Ion (Abel).

The velocity of the catalyzed reaction, given by the first step, must again be:

$$\frac{dx}{dt} = 0.667(a - x)c,$$

where c refers to the concentration of iodide ions, maintained constant by the successive reactions. The total reaction in presence of the catalyst may then be obtained from the sum of the catalyzed and uncatalyzed reactions, which, after simplification is therefore:

$$\frac{dx}{dt} = 1.53\left[(b - x) + \frac{0.67}{1.53}c\right](a - x).$$

It is apparent from Fig. 6, which contains the time curves of the uncatalyzed, and the calculated and observed catalyzed reactions, that the calculation is satisfactory at all points.

Selective Catalysis: While, in the foregoing example, with hydrogen peroxide alone, or catalyzed by iodide ions, thiosulphate was exclusively converted to tetrathionate, the reaction may be very strongly catalyzed in acid solution by molybdic acid in the direction:

$$4H_2O_2 + S_2O_3'' = 2SO_4'' + 2H^{\cdot} + 3H_2O.$$

We have here then, a typical case of selective catalysis or *direction* of the course of reaction.

The theory of intermediate reactions can easily explain such a phenomenon if it is assumed that an entirely new intermediate is formed, different from the collision complex, $H_2O_2 \cdot S_2O_3''$, of the uncatalyzed reaction and from the IO′ of the catalyzed reaction, which consequently can have an altogether different effect on the thiosulphate.

The reaction was discovered and investigated by Abel,[117] who assumed the intermediate to be *permolybdic acid.* The velocity equation, measured at 25° was,

$$\frac{dx}{dt} = [1600 + 3.5 \times 10^7[H^{\cdot}]\,]\,[MoO_3]\,[S_2O_3''].$$

The reaction must be carried out in buffered solution because of the strong dependence on hydrogen ion concentration, and since hydrogen ions are furnished by the reaction itself.

The velocity is independent of one of the substrates (zero order), namely, hydrogen peroxide, which means (see p. 76) that the intermediate is of the Arrhenius type and its concentration corresponds approximately to that of the catalyst. Now Brode [118] has already pointed out to similar purpose that permolybdic acid is only slightly decomposed into molybdic acid and hydrogen peroxide. It can be assumed, therefore, that the total catalyst (MoO_3) is bound to the substrate (H_2O_2) as permolybdic acid.

There now remains to be explained the influence of hydrogen ions and the form in which it enters the equation.[119] We may either suppose that the hydrogen ion in its turn catalyzes the permolybdate ion-thiosulphate ion

[117] E. Abel, *Z. Elektrochem.*, **18**, 705 (1912);
E. Abel and G. Bawm, *Monatsh. f. Chem.*, **34**, 425 (1912).
[118] J. Brode, *Z. physik. Chem.*, **37**, 257 (1901).
[119] E. Abel, *Monatsh. f. Chem.*, **34**, 821 (1912).

reaction, which can then proceed with *and* without it:

$$5MoO_5'' + S_2O_3'' = 5MoO_4'' + 2SO_4'',$$

$$\frac{dx}{dt} = 1600[MoO_3]\,[S_2O_3''],$$

$$5MoO_5'' + S_2O_3'' + H^{\cdot} = 5MoO_4'' + 2SO_4'' + H^{\cdot},$$

$$\frac{dx}{dt} = 3.5 \times 10^7[H^{\cdot}]\,[MoO_3]\,[S_2O_3''],$$

or assume that an equilibrium exists:

$$H^{\cdot} + MoO_5'' \rightleftarrows HMoO_5',$$

that is, that the so-called hydrogen ion catalysis is fundamentally an Arrhenius mechanism, and that the primary stage of dissociation as well as the secondary stage acts on S_2O_3'' and, indeed, considerably faster, since the latter can only be present in relatively small amounts because of proportionality with the concentration of MoO_3.

The uncatalyzed formation of tetrathionate still proceeds alongside the sulphate formation catalyzed by molybdic acid, according to the equation

$$\frac{dy}{dt} = 1.53(a-x-y)^2$$

where x is the amount of tetrathionate formed, y is the sulphate formed, and a represents the initial concentrations of peroxide and thiosulphate which are assumed to be the same. We had, for the molybdic acid catalysis:

$$\frac{dx}{dt} = [1600 + 3.5 \times 10^7[H^{\cdot}]\,]\,[MoO_3]\,(a-x-y).$$

After division, integration, and transformation, the yield in sulphate is given by:

$$\frac{y}{a} = \frac{230}{m} \log \frac{1+m}{1+rm},$$

where $m = \dfrac{1.53}{[1600 + 3.5 \times 10^7[H^{\cdot}]\,]\,[MoO_3]}$, and $r = \dfrac{a-x-y}{a}$.

The yields calculated in this way agree quantitatively with the values found by experiment, indicating that the catalyzed and uncatalyzed reactions occur simultaneously and independently, and, therefore, that the catalyst has opened an entirely new way of reaction.

Besides the selectivity in which the catalyst directs a given substrate along a particular path, there is often a more complex specificity, especially

characteristic in catalysis, namely, that a given catalyst prefers for one and the same reaction one or a few of various, generally similar, substrates.

The case of optical specificity is especially important because it can be understood. The competing substrates do not differ in chemical and physical properties but only in their optical configurations. This specificity plays a quite considerable rôle among organisms, where it is a property of enzyme catalysts. It occurs also in heterogeneous catalysis. It was discovered in a catalytic reaction in solution, the elimination of carbon dioxide from camphoric acids in organic solvents, either *d* or *l* acids being preferentially decomposed yielding the corresponding camphor.[119a]

The different velocities of decomposition of the optical antipodes arise from the asymmetric nature of the intermediate compound between the catalyst and substrate. These intermediates differ also in chemical properties such as decomposition velocities. It has not yet been decided whether the differences in carbon dioxide elimination are due to van't Hoff intermediates or to differences in the formation-decomposition equilibria of Arrhenius-intermediates. At any rate, for enzymic specificity, both equilibrium concentration and decomposition velocity are, in the case of Arrhenius intermediates, specific for a particular configuration.

Promoter Action with Two Catalysts: The various modes of reaction possible in a given mixture are not always independent of one another. If that were the case, the resultant velocity in the presence of two or more catalysts would simply be equal to the sum of the velocities for each catalyst acting separately. This is, of course, very frequently the case, especially when hydroxyl and hydrogen ions and water molecules are the catalysts. Brode [118] found that the following catalyst pairs behave similarly in the oxidation of iodide ions by hydrogen peroxide: molybdic acid with iron, copper, or tungstic acid, and tungstic acid with copper. The accelerating effect of a mixture of two such catalysts is additive, therefore, and can be calculated from the separate effects of the components by the mixture rule.

This is not always the case, however. An added substance often reduces the efficiency of a catalyst; for example, tungstic acid efficiency in the above mentioned cases is reduced by small amounts of iron, owing to the formation of an inactive complex. Such " diminution " will be specially dealt with under the heading of " negative catalysis." The reverse case, however, in which the efficiency of a mixture of catalysis exceeds the additivity to be expected from the independent effect of each catalyst, is also very frequent.

[119a] G. Bredig and K. Fajans, *Ber.*, **41**, 752 (1908); K. Fajans, *Z. physik. Chem.*, **73**, 54 (1910); G. Bredig and Minaeff. Festschr. Hundertjahrfeier Tech. Hochsch. Karlsruhe, 1925, and literature there cited.

The term ' promotion ' was first used in connection with this phenomenon by Brode [118] in 1901. We shall see, later, that other expressions are also in use in heterogeneous catalysis, where the effect is of the greatest technical importance.

In the first place, we shall not consider the dependence on p_H displayed by many catalysts, in which the hydrogen ion could be regarded as a promoter (see the catalysis of the hydrogen peroxide-thiosulphate reaction by molybdic acid on p. 82). The acid-base catalysis investigated by Lowry (see pp. 68 and 121), where at least one of the components possesses by itself no catalytic effect whatever will be likewise disregarded.

The first observation of promotion appears to have been made by Price [119b] in 1898. He studied the bimolecular reaction occurring in neutral and acid solution between persulphate and iodide:

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

or

$$S_2O_8'' + 2I' = 2SO_4'' + I_2.$$

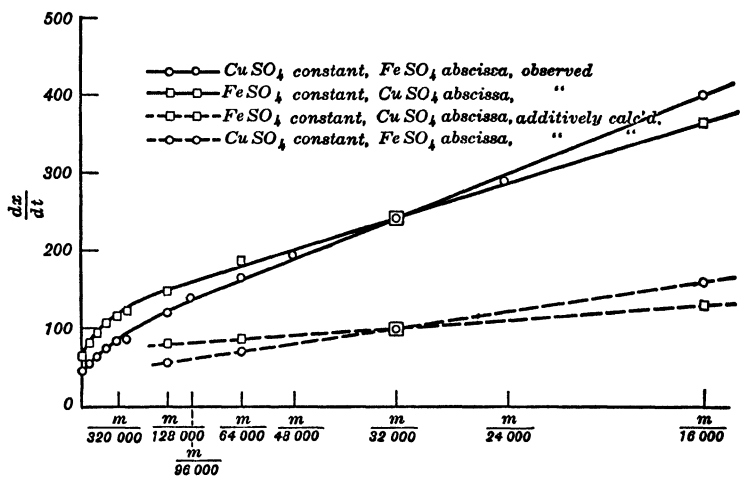


FIG. 7. Acceleration of the Persulphate-Iodide Reaction by Iron and Copper (Price).

It is very strongly accelerated by ferrous and ferric ions in proportion to their concentration, the iron evidently acting as a carrier by the ready interchange of charge. Copper is less efficient, being somewhat inhibited in acid solution, but otherwise behaves similarly, for the same reason. If both catalysts are added to the reaction mixture, however, the effect far surpasses the sum of the separate effects, as is apparent from Fig. 7. Also, the func-

[119b] T. S. Price, *Z. physik. Chem.*, **27**, 474 (1898).

tional connection between the velocity and the concentration of one catalyst at constant concentration of the other, is now very characteristically altered.

If, originally, the velocity was proportional to the catalyst concentration, i.e., we had the limiting case with very small concentration of intermediate substance (e.g. cuprous ion), the " order " with two catalysts varies between zero and one. This means that the concentration of one intermediate has now become commensurable with that of one of the remaining partners (probably with that of the other intermediate). The curves directly correspond to what would be expected according to the Spitalsky [112] interaction terms. The promotion is so sensitive that, in N/32,000 $Fe^{\cdot\cdot}$, for example, the velocity is increased about 15% by the addition of N/2,560,000 $Cu^{\cdot\cdot}$.

We are indebted to Brode [118] for a very exhaustive investigation of a closely related process, already quite familiar to us, the oxidation of iodide ions by hydrogen peroxide. Although the presence of hydrogen ion is required as a catalyst, very interesting catalytic phenomena may nevertheless be observed at constant p_H. As in the analogous persulphate reaction, we again find characteristic promotion by ions of iron and copper. The acceleration is proportional to the iron concentration (after deducting that due to $H^{\cdot}$), and an addition of even 0.0002N copper brings about a considerable increase in the proportionality factor. Copper alone is likewise effective, although 100 times weaker in this case, when present in appreciable amount. On the other hand, its promotive effect on the iron catalysis is still noticeable in N/100,000 solution. The influence of constant copper concentration with increasing iron concentration is shown in Fig. 8.

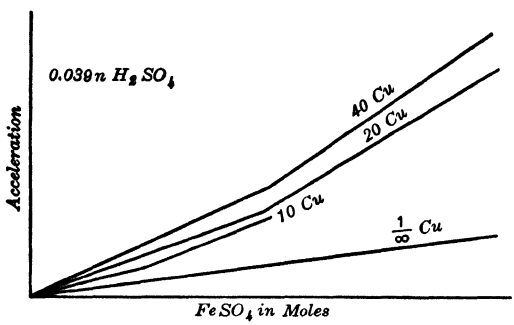


FIG. 8. Acceleration by Copper of the Hydrogen Peroxide-Iodide Reaction Catalyzed by Iron (Brode).

In order to ascertain the dependence on the copper concentration, experiments were carried out with constant concentration of iron and varying additions of copper. The results at different iron concentrations are shown in Fig. 9. It is evident that, this time, the dependence on copper again varies between zero and first order, unlike the dependence on iron.

Brode discussed the possibility of the promotion being due, as Noyes had

suggested, to each catalyst " activating " only one of the reactants, converting it into a reactive intermediate. As we make use of this possibility again in heterogeneous catalysis (see p. 304), we shall reproduce his argument. If this theory is correct, it is easy to show that, in the case of three catalysts, promotion must always be found either in none or two of their three double combinations. If one chooses so to explain the observed effect that iron, for example, activates the hydrogen peroxide (as is probable), and copper the iodine, combinations of these with molybdic acid, also investigated by Brode, give the following: since iron and copper promote, and iron and molybdic acid are additive, as already mentioned (p. 82), copper and molybdic acid should promote, since the molybdic acid, like iron, would then activate the peroxide. This does not agree with the additivity shown by copper and molybdic acid, which is rather noteworthy, for Brode was able to show, by various measurements, that molybdic acid actually reacts primarily with hydrogen peroxide to give per-acid. Brode concluded, therefore, that, besides the uncatalyzed way of reaction, and the paths via copper and iron, a new reaction path induced by iron and copper must also be present.

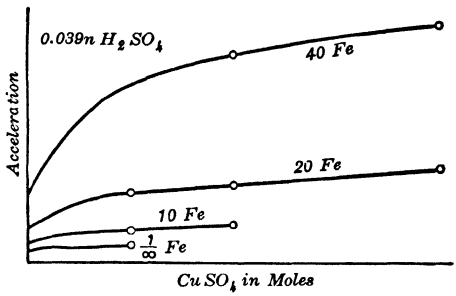


FIG. 9. Acceleration by Iron of the Hydrogen Peroxide-Iodide Reaction Catalyzed by Copper (Brode).

The observed curves can, in fact, be obtained from such an assumption by considerations similar to those which Spitalsky has already worked out for promotion. We assume the following scheme:

$$\begin{aligned} &\text{uncatalyzed:} && A \rightarrow B, \\ &\text{with one catalyst:} && A + C_1 \rightleftarrows Z_1 \\ & && Z_1 \rightarrow B + C_1, \\ &\text{with both catalysts:} && Z_1 + C_2 \rightleftarrows Z_2, \\ & && Z_2 \rightarrow B + C_1 + C_2. \end{aligned}$$

Making Spitalsky's assumptions, this gives:

$$\frac{d[B]}{dt} = \underset{\substack{\text{without}\\ \text{catalysis}}}{k_0[A]} + \underset{\substack{\text{with Cu}\\ \text{alone}}}{\frac{k_1K_1[C_1][A]}{1 + K_1[A]}} + \underset{\substack{\text{with Cu}\\ \text{and Fe}}}{\frac{k_2K_1K_2[C_1][C_2][A]}{1 + K_1[A] + K_2K_1[C_1][A]}}$$

If C_1, and consequently the copper, is maintained constant, and the small velocity of the copper catalysis alone is taken into consideration, proportionality with the iron, C_2, is obtained. If, on the other hand, iron is constant, the last term, which has C_1 in the denominator, gives a variable order with respect to copper. The catalysis by iron alone is not considered. It is intended to be contained in k_0, which then becomes proportional to the iron concentration down to quite small additions. The simple result therefore describes the promotion curves correctly, thereby showing that, in homogeneous systems, these effects can be adequately explained on the basis of intermediate reactions. A detailed theory will not be proposed, since the intermediates are more likely to be charged ions than the compound Z.

Yet a third case of copper-iron promotion has been found by Schilow and Buligin,[120] namely, the reaction between sulphite and persulphate:

$$SO_3'' + H_2O + S_2O_8'' \rightarrow 3SO_4'' + 2H^{\cdot}.$$

The authors also represent this process as occurring by three parallel paths, catalyzed by iron, copper, and by iron-copper respectively. Although the kinetics do not allow any special conclusions to be drawn regarding the nature of these paths, it is fairly certain that the ions catalyzed the oxidation by intermediary valence changes.

An example illustrating that this kind of mechanism is not confined to aqueous solution, is the catalysis of the Kjeldahl process investigated by

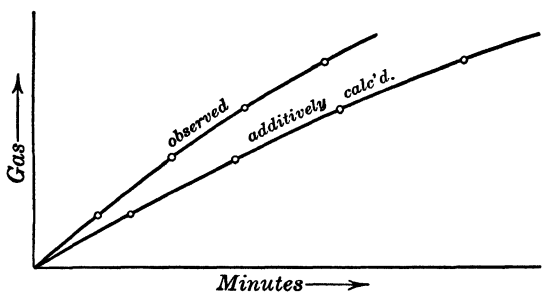


FIG. 10. Acceleration of the Kjeldahl Reactions by Copper and Mercuric Ions (Bredig and Brown).

Bredig and Brown.[121] They studied the kinetics of the oxidation of aniline to ammonium sulphate and of naphthalene of phthalic acid in concentrated sulphuric acid, by collecting the products, sulphur dioxide and carbon

[120] N. Schilow and N. Buligin, *Chem. Ztg.*, **37**, 512 (1913).

[121] G. Bredig and J. W. Brown, *Z. physik. Chem.*, A **6**, 502 (1903).

dioxide, which are formed. The reactions are approximately first order and can both be catalyzed by copper salts and by mercuric salts. In this case also, these salts are more effective when present simultaneously than separately. The decomposition-time curve expected from the additive effects is shown beside the experimental curve in Fig. 10.

Apparent promotion or retardation due to mutual reaction of the catalysts is not to be confused with genuine deviations from additivity such as the above. Thus, it is not to be expected that the addition of NaOH to HCl will promote mutarotation ascribed to OH' and $H^{\cdot}$. The catalysis of the decomposition of hydrogen peroxide by chromate-dichromate mixture is an example of this kind. The chromate catalysis proceeds according to:

$$\frac{dx}{dt} = 460[CrO_4''] [H_2O_2],$$

and the dichromate catalysis according to:

$$\frac{dx}{dt} = 137{,}000[Cr_2O_7''] [H_2O_2].$$

Spitalsky had observed that, in mixtures of both salts, the resultant velocity cannot be obtained from the above expressions by the mixture rule, but that a minimum (diminution) appears at a given composition of the mixture. Meanwhile, Riesenfeld [122] was able to show that OH' ions are formed by the hydrolysis of the chromic acid, which then convert the dichromate into the less effective chromate according to:

$$Cr_2O_7'' + 2OH' \rightleftarrows 2CrO_4'' + H_2O.$$

Since the hydrolysis constant of chromic acid and the constant of the above equilibrium (3.4×10^{15}) are known, the true concentration of chromate and dichromate ions can be calculated, and when this is done, the mixture rule is strictly obeyed.

[122] E. H. Riesenfeld, *Z. anorg. Chem.*, **74**, 48 (1912).

CHAPTER VI

HOMOGENEOUS CATALYSIS IN SOLUTION. II

Fundamentals of Ion Catalysis

In the examples which have so far been dealt with, we have frequently come across ions such as I', MoO_4'', $Fe^{\bullet\bullet}$, $Cu^{\bullet\bullet}$, as catalysts in solution. Owing to the predominant rôle of water as a solvent in nature, the catalyst and, possibly, the active substrate are represented by ions in the vast majority of catalytic processes which have been investigated. In the treatment of catalysis in solution, therefore, we shall be occupied almost exclusively with ion catalysis. For similar reasons, the ions of water itself are unique among the catalyzing ions, as regards efficiency. This circumstance, in combination with the widespread occurrence of high reaction velocities in ionic reactions, has even led to the tacit assumption (see Abel's criticism of this) [123] that catalysis occurs by ions in preference to molecules. The conception was extended to heterogeneous catalysis but, as we shall see, it has been modified by the facts.

Proportionality to Ion Concentration: Contemporaneously with the original formulation of the Arrhenius theory, Ostwald was engaged in an investigation of the catalytic effect of acids. He studied the velocity of ester hydrolysis [124] and the inversion of cane sugar [125] in the presence of widely different acids. On the basis of numerous measurements of his own as well as on previous measurements, he arrived at the noteworthy result that the velocity of both reactions at equal concentrations of different acids was proportional to the conductivity of the acids. In particular, he observed that acids of the same conductivity produced the same velocities and, indeed, when suitably adjusted, the same for both reactions. The following table has been taken from Ostwald's collected results. The unimolecular constant is given for the inversion, and the square root of the bimolecular constant (for concentration in mols per litre) for the hydrolysis reaction. Both have constant values and were termed by

[123] E. Abel, *Z. Elektrochem.*, **9**, 938 (1913).
[124] W. Ostwald, *Z. physik. Chem.*, **1**, 78 (1887).
[125] W. Ostwald, *J. Prakt. Chem.*, **29**, 401 (1884).

TABLE VI — CATALYTIC ACTIVITIES OF ACIDS

Acid	k (inversion)	$\sqrt{k}$ (ester hydrolysis)	Conductivity
HCl	24.12	21.87	367
HNO_3	22.06	21.87	363
$HClO_3$	22.78	22.61	355
$C_6H_5SO_3H$	23.94	22.82	326

Ostwald " affinity constants " of the respective acids. From the fact that the velocity was independent of the anion of the acid and proportional to the conductivity (degree of dissociation), it was naturally concluded that the *hydrogen ion*, was the effective constituent of all acids and that the catalytic effect was proportional to its concentration. These observations lent strong support at the time to the new and strongly opposed theory of dissociation.

Soon afterwards, similar measurements were undertaken or originated by Arrhenius (e.g. Ref. 13). Although he found the most important of the deviations which have recently become significant,[126] proportionality with hydrogen ion concentration still appeared to be a well established rule, especially at low acid and low total concentrations. This conclusion was supported by the great series of investigations carried out in the years which followed.[127] Both reactions were even recommended for the determination of hydrogen ion concentration. We saw in the preceding chapter a similar sort of dependence demonstrated in connection with the catalytic effects of a series of other ions, and observed that the simple theory of intermediate reactions generally sufficed. Proportionality with ion concentration may, therefore, be regarded as an elementary rule of homogeneous catalysis, exceptions to which provide the material for further research.

The Effective Form of the Catalyst: We may now inquire as to the form in which the catalyst, and the hydrogen ion in particular, is active. At the outset, we may assume the existence side by side in the solution, of different, more or less solvated, or free modifications of the ions whose concentrations must all be proportional to one another. Thus, Lapworth [128] and also Rice [129] suggested that only the free unhydrated hydrogen

[126] S. Arrhenius, *Z. physik. Chem.*, **28**, 319 (1899).

[127] See Register of *Z. physik. Chem.*, **1–50**, under " Zucker-inversion," " Esterverseifung."

[128] A. Lapworth, *J. Chem. Soc.*, **93**, 2163 (1908); **93**, 2187 (1908); **107**, 857 (1915).

[129] F. O. Rice, *J. Am. Chem. Soc.*, **45**, 2808 (1923).

ion is effective. However, as Brönsted [130] points out, we can suppose that the free hydrogen ion does not exist to any extent in solution on account of its high heat of hydration, while it appears from atomic theory (Fajans, Grimm) that the free hydrogen ion so easily deforms and penetrates the electron shells of all solvents, that it is buried in solvent molecules. We have, therefore, to examine whether the solvated hydrogen ion can be effective catalytically. In the special case in which the solvent is the substrate at the same time (hydrolysis in water, such as inversion and ester hydrolysis; alcoholysis and esterification in alcohols) the question resolves itself into a problem of whether catalysis is negotiated by an intermediate compound of hydrogen ion-substrate.

An extremely fruitful series of researches by H. Goldschmidt, extending over many years, has yielded definite and important information in this direction, leading to the conception that the effective agent is the hydrogen ion solvated with the substrate, but that ions otherwise solvated are not active or only active insofar as they are in equilibrium with the ion-substrate complex.

Goldschmidt investigated the velocity of esterification of different acids and alcohols catalyzed by other, and also the same, acids in the esterifying alcohol as solvent. He found, first of all,[131] that the reaction, in itself bimolecular, occurs pseudo-unimolecularly, because the concentration of alcohol is practically constant. For example, he obtained the following value of the velocity constant, first order with respect to the acid concentration:

TABLE VII — CATALYTIC ACTIVITIES OF ACIDS IN ETHYL ALCOHOL

Acid esterified	Alcohol	Catalyst acid	k
Benzoic acid.....	abs. ethyl alcohol	HCl, HBr	0.0428
Benzoic acid.....	89.7% ethyl alcohol	HCl, HBr	0.0016
Benzoic acid.....	abs. ethyl alcohol	Picric acid	0.00283
Phenylacetic acid	abs. ethyl alcohol	HCl	3.3

The low value for picric acid as compared with the mineral acid, is accompanied by a considerably smaller conductivity of this acid in alcohol, whence it would appear that the catalysis is due to the dissociated portion of the acid catalyst. On the other hand, addition of water increases dissociation, so that the strong inhibition by water in the case of mineral

[130] J. Brönsted, *Trans. Faraday Soc.*, **24**, 630 (1928).
[131] H. Goldschmidt, *Ber.*, **28**, 3218 (1895).

acids seems rather to support catalysis by the undissociated part. However, the increase in conductivity does not correspond to the decrease in velocity by any means, and this possibility is not substantiated. At the time, the catalyst was supposed to be the hydrogen ion.

In the following year [132] this view received strong support from the fact that the velocity was decreased by addition of salts of the same anion to weakly catalytic acids, as, for instance, p-toluidine picrate to picric acid. This is shown in the accompanying Table VIII. The values given

TABLE VIII — SALT EFFECT IN ACID CATALYSIS

Salt addition	k
0 : 1	0.0187 to 0.0147
1 : 1	0.0086 to 0 0082
2 : 1	0.0072 to 0.0066

under "k" represent the limits occasioned by the formation of water. The inhibition by water is partly specific, as above — an effect which subsequently becomes important — and is partly concerned with an increase in the salt dissociation. As the exact dissociation ratios of acid and salt were unknown at the time, it was impossible to deduce the salt inhibition quantitatively. It was, nevertheless, quite evident that the dissociated portion of the picric acid is effective.

At the same time, it was also found that trichloracetic acid catalyzes its own esterification, that is, the esterification proceeds according to the second order without addition of foreign acid. The velocity of "self esterification" could be represented by:

$$\frac{dx}{dt} = k(a - x)^2 \cdot \alpha,$$

where α is the degree of dissociation of trichloracetic acid, again indicating that ester formation is effected by a fragment common to all acids, and therefore by the hydrogen ion.

In collaboration with Sunde,[133] Goldschmidt obtained further support for this view by comparing the catalytic efficiency of acids with their degree of dissociation in anhydrous alcohol (lime distilled, 0.2 to 0.3% H_2O), under reproducible conditions. The following results were obtained:

[132] H. Goldschmidt, *Ber.*, **29**, 2208 (1896).
[133] H. Goldschmidt and E. Sunde, *Ber.*, **39**, 711 (1906).

TABLE IX — RELATIVE ACTIVITIES OF ACIDS

Acid esterified	$\frac{k \text{ hydrochloric acid}}{k \text{ picric acid}}$	$\frac{k \text{ picric acid}}{k \text{ trichloracetic acid}}$	$\frac{k \text{ trichloracetic acid}}{k \text{ dichloracetic acid}}$
Phenylacetic acid	8.8	8.6	—
Acetic acid	10.5	10	4.4
Ratio of the degrees of dissociation of the catalyst acids	5.5	6.4	4.5

In spite of the variation in the numerical values, it is clear that the more strongly dissociated acid is always the better catalyst. This was shown more exactly in a later paper,[134] as the following Table X shows:

TABLE X — CONDUCTANCE-CATALYSIS RELATIONS

	0.1 N. solution				
	HCl	Picric acid	Trichlor-acetic acid	Trichlor-butyric acid	Dichlor-acetic acid
Conductivity	34.1	3.56	0.34	0.12	0.076
k for esterification of formic acid	——	3.5	0.354	0.101	0.063

Goldschmidt and Sunde also found that the influence, upon the velocity, of the suppression of dissociation of the catalyst acid by the substrate acid shows the expected sequence with the strength of the two acids. On the whole, the velocity increases rather more slowly than the concentration of the catalyst acid, as would be expected in a catalysis by hydrogen ions. In spite of various deviations which had already become evident in this work, and which will be discussed in another place, the results obtained up to that time were very much in favor of catalysis by hydrogen ions.

The problem of confirming this assumption quantitatively was connected with the question of the rôle of solvation referred to at the beginning of this section. The inhibition of the reaction by water, which has already been mentioned, offered the key to the solution of the problem.

Goldschmidt and Udby [135] showed first of all, that it cannot be decided

[134] H. Goldschmidt, *Z. Elektrochem.*, **15**, 4 (1909).

[135] H. Goldschmidt and O. Udby, *Z. physik. Chem.*, **60**, 728 (1907).

from the kinetics of the hydrolysis itself whether the hydrogen ion forms an Arrhenius intermediate compound with the acid or with the alcohol, since its concentration, as long as it is small, is always proportional to the product of the components, and both assumptions, therefore, lead to the same result. On the other hand, the circumstances are different as regards the influence of water. It is assumed that water enters into competition with the substrate, by the formation of a compound with the hydrogen ion, the hydroxonium ion $H_3O^{\cdot}$. Two possibilities may be examined.

I. If the intermediate in the catalysis is a compound with the acid, we should have the following equation:

$$\begin{array}{ccccccc} CH_3COOH \cdot H^{\cdot} & + & H_2O & \rightleftarrows & CH_3COOH & + & H_3O^{\cdot} \\ \xi & & n+x-\eta & & a-x-\xi & & \eta \end{array}$$

The expressions written beneath the formulae represent the concentrations of the respective substances, since a is the initial concentration of acid, x the change taking place (acid removed = water formed), and n is the concentration of the water added. It is further supposed that:

$$\xi \ll a-x \quad \text{and} \quad \eta \ll n+x.$$

Without the addition of water, we should only have to consider the equation

$$\begin{array}{ccccc} CH_3COOH & + & H^{\cdot} & \rightleftarrows & CH_3COOH \cdot H^{\cdot}, \\ a-x-\xi & & c & & \end{array}$$

from which it follows that:

$$\xi = K(a-x)c.$$

By the competition of water, ξ is reduced by the amount of hydrogen ion combining with the water, thus:

$$\xi = Kc(a-x)-\eta.$$

Now, we obtain from the first equilibrium equation involving water

$$\eta = \frac{\xi(n+x)}{r(a-x)},$$

where r is the hydrolysis constant of the acid-hydrogen ion. This gives:

$$\xi = -\frac{(a-x)^2 Krc}{r(a-x)+n+x}.$$

Representing the (constant) alcohol concentration by b, we obtain for the reaction velocity

$$\frac{dx}{dt} = kbKrc\frac{(a-x)^2}{r(a-x)+n+x}$$

and integrating,

$$kbKrct = \frac{n+a}{a}\frac{x}{a-x} - (1-r)\,ln\frac{a}{a-x}.$$

This would require the relative change after equal times to be independent of the acid concentration a, since $\frac{n+a}{a}$ approaches constancy. In reality, however, a diminishing change was found with increasing a, and the scheme is consequently untenable.

II. What is the result when the hydrogen ion forms the interacting complex *with the alcohol?* Its concentration is:

$$\xi = Kbc - \eta$$

where η is determined by the equilibrium:

$$\begin{array}{ccccc} C_2H_5OH \cdot H^{\cdot} & + & H_2O & \qquad & C_2H_5OH + H_3O^{\cdot}. \\ \xi & & n+x-\eta & & b \qquad\qquad n \end{array}$$

Goldschmidt and Udby then obtain:

$$\eta = \frac{\xi(n+x)}{r}$$

and

$$\xi = \frac{Kbcr}{r+n+x},$$

and by introduction of the acid concentration $a - x$:

$$\frac{dx}{dt} = \frac{kKbcr(a-x)}{r+n+x}$$

which gives the decrease in velocity which is observed with increasing water concentration, and, as Goldschmidt and Udby show, it agrees with the more than proportional rise in velocity with the catalyst concentration (when η is not neglected in comparison with $n + x$).

The integrated form of the expression is

$$kKbcrt = (n + r + a)\,ln\frac{a}{a-x} - x.$$

This manifestly gives a decreasing relative change with increasing a. Constant values of $kKbcr$ were obtained in the numerous experiments which Goldschmidt and Udby made with different concentrations of water, catalyst acid, and substrate acid. All measurements can be reproduced if the hydrolysis constant r of the alcohol-hydrogen cation is assumed to be 0.15 (referred to 40 per cent dissociation of HCl in alcohol).

This constant r is entirely independent of the nature of the substrate acid, which is the best evidence in favor of the conclusion that the latter is not contained in the intermediate. Soon afterwards, Goldschmidt [134] established that the catalyst does not affect the form of the velocity curve but only its magnitude (see also p. 99). He found, furthermore, that the same requirements are fulfilled with alcohols other than ethyl alcohol. In such cases, different values of r are to be expected, since it is the alcohol that takes part in the equilibrium. Actually Goldschmidt found the following values for r:

methyl alcohol	0.21
ethyl alcohol	0.15
isobutyl alcohol	0.088

The conclusion that the hydrogen ion forms an intermediate compound with alcohol can, therefore, no longer be avoided. In a paper in collaboration with Udby,[136] Goldschmidt inquires whether this is a true Arrhenius intermediate, or whether the velocity is determined by its rate of formation, but a definite decision cannot be reached, since, as we shall see later, a circumstance is present which complicates the theory. The latter assumption, nevertheless, does not appear to fit the experiments so well as the former.

The validity of Goldschmidt's results has so far been maintained, as, for example, in the investigation in 1929 by Goldschmidt, Haaland and Sommerschild Melbye on the proportionality of formic acid esterification to hydrogen ion concentration, using different catalyst acids [137] and they have been notably confirmed by the investigation of another catalysis in alcohol, the alcoholysis of diazoacetic ester, by Bredig and his collaborators.

We shall consider first the hydrolysis of the ester, which was described and investigated by W. Fraenkel.[138] It takes place according to the equation:

$$\begin{array}{l} H-C-COO\cdot C_2H_5 + H_2O \rightarrow HO-CH_2-COO\cdot C_2H_5 + N_2 \\ \quad\diagup\diagdown \\ \quad N=N \end{array}$$

and therefore may be conveniently followed kinetically by measurement of the nitrogen evolved. The velocity is found to be strictly proportional to the concentration of ester and hydrogen ions, analogous to ordinary ester hydrolysis. The same catalytic efficiency is obtained for the hydrogen ion, calculated from Ostwald's dissociation constants in the case of weak acid

[136] H. Goldschmidt and O. Udby, *Z. physik. Chem.*, **70**, 627 (1910).

[137] H. Goldschmidt, H. Haaland, and R. Sommerschild Melbye, *Z. physik. Chem.*, A **143**, 278 (1929).

[138] H. W. Fraenkel, *Z. physik. Chem.*, **60**, 202 (1907).

catalysts such as acetic acid, fumaric acid, succinic acid, and *m*-nitrobenzoic acid, as that derived from the total acid concentration in the case of strong acids in alcohol (nitric acid and picric acid). The reaction is also inhibited by salts with a common ion, in agreement with the calculated suppression of dissociation. It is therefore another example of a reaction catalyzed by hydrogen ions in proportion to their concentration.

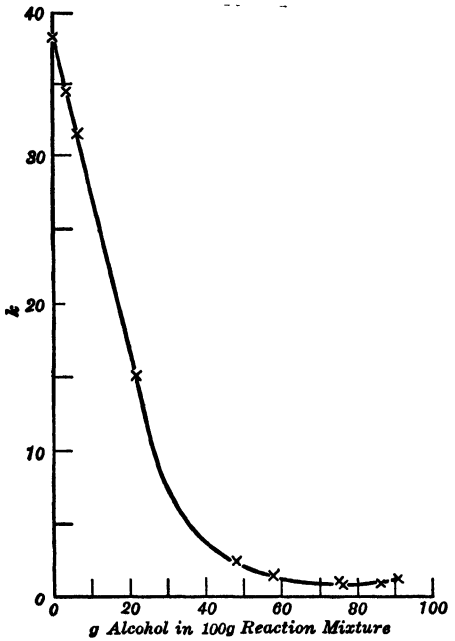


FIG. 11. Inhibition of Diazoacetic Ester Hydrolysis by Alcohol (Bredig and Fraenkel).

Investigation of the reaction with alcohol instead of water, again leads to a successful explanation of the phenomena. Ethyl alcohol first *inhibits* the hydrolysis up to an alcohol concentration of 90% as shown in Fig. 11. An increasing evolution of nitrogen takes place again at higher concentration, and this occurs very rapidly in absolute alcohol. Analysis shows that the alcoholysis proceeds according to the equation:

$$\begin{array}{l} H-C-COO\cdot C_2H_5 \\ \quad\diagdown\diagup \\ \quad N=N \end{array} + C_2H_5OH \rightarrow C_2H_5-\underset{\displaystyle OH}{\underset{|}{CH}}-COO\cdot C_2H_5 + N_2.$$

In comparison, the hydrolysis completely disappears at water concentrations below 0.6%. The alcoholysis is also catalyzed by acids, but not in such a simple fashion as the hydrolysis. Like the Goldschmidt esterification, it is inhibited by water, a feature which becomes of great interest later. In 0.00909 *N* picric acid solution, for example, 0.18% water reduced the velocity by about 22%.[139]

Millar [140] (see also Bredig) [141] has carried out kinetic measurements of this reaction with a large number of catalyst acids. At the beginning

[139] G. Bredig and H. Fraenkel, *Ber.*, **39**, 1756 (1906).
[140] W. S. Millar, *Z. physik. Chem.*, **85**, 129 (1913).
[141] G. Bredig, *Z. Elektrochem.*, **18**, 535 (1912).

of the reaction, where the slow esterification of the catalyst acid can be neglected, and, in addition, where x is small compared with n, the Goldschmidt relationship:

$$\frac{dx}{dt} = \frac{kKbcr(a-x)}{r+n}$$

holds approximately. This can also be written:

$$n = \frac{1}{k_{\text{uni}}} \cdot kKbcr - r$$

(k_{uni} is the formal first order " constant ").

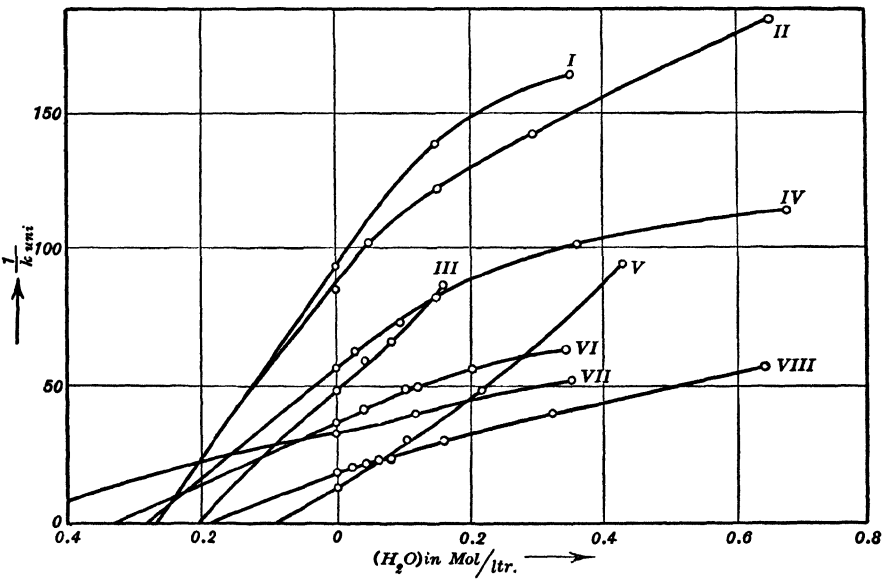


FIG. 12. Inhibition by Water of the Decomposition of Diazoacetic Ethyl Ester in Alcohol (without Correction for Dissociation) (Bredig and Millar).

Curve		*Catalyst*	*Curve*		*Catalyst*
I.	0.0909	N Trinitrobenzoic Acid	V.	0.00182	N Sulphosalicylic Acid
II.	0.0455	N Trichloracetic Acid	VI.	0.182	N Trichloracetic Acid
III.	0.00227	N Picric Acid	VII.	0.0909	N Trichlorbutyric Acid
IV.	0.0909	N Trichloracetic Acid	VIII.	0.00909	N Picric Acid

According to this equation, $1/k_{\text{uni}}$ should increase linearly with n and the curves of all acids, extrapolated backwards, should meet the horizontal axis when $n = r$. Fig. 12 shows how far this is the case. It is evident that all the curves are of the expected type, but that there is considerable

deviation from linearity and from a standard limiting value. In other experiments, $r = 0.26$ (0.15) for ethyl alcohol, 0.57 (0.21) for methyl alcohol, and 0.12 (0.088) for isobutyl alcohol. The Goldschmidt values, which should be identical with these, are given in parenthesis.

Now the concentration of hydrogen ion which enters the Goldschmidt derivation, is not equal to c, the total concentration of catalyst acid, as assumed, but equal to the latter multiplied by the degree of dissociation of the acid. In fact, Goldschmidt had made use of this correction in the determination of r.

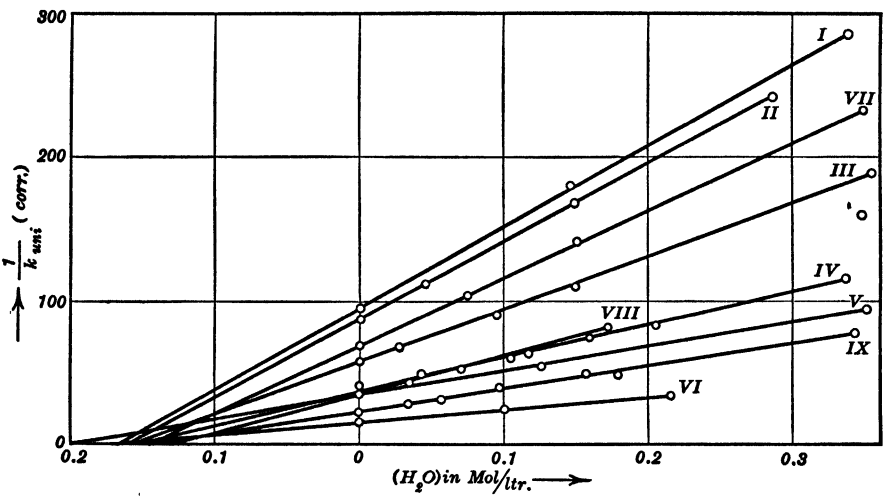


FIG. 13. Inhibition by Water of the Decomposition of Diazoacetic Esters in Alcohol after Correction for Dissociation of the Catalyst Acids (Bredig and Millar).

Curve	*Catalyst*	*Substrate*
I.	0.0909 N Trinitrobenzoic Acid	Ethyl Ester
II.	0.0455 N Trichloracetic Acid	" "
III.	0.0909 N " "	" "
IV.	0.182 N " "	" "
V.	0.0909 N Trichlorbutyric Acid	" "
VI.	0.00182 N Sulphosalicylic Acid	" "
VII.	0.0909 N Trichloracetic Acid	Methyl Ester
VIII.	0.00455 N Picric Acid	" "
IX.	0.00909 N " "	" "

This was investigated by Millar, who calculated the degree of dissociation of the different acids for different additions of water from the observed conductivity, assuming the conductivity at infinite dilution to be independent of the water addition, since dissociation is then complete. If this

correction is applied to $kKbc$, and $kKbc\lambda_n/\lambda_\infty$ be written instead, Fig. 13 is obtained. The deviations have now almost disappeared and agreement with Goldschmidt's r for ethyl alcohol = 0.15 is obtained (see p. 104 for the meaning of the remaining deviations). It is clear, therefore, that we have here another example in which the hydrogen ion activates the alcohol by formation of a complex.

The "Dual" Theory of Catalysis: The next important advance in our knowledge of acid-base catalysis was initiated by the observation of deviations from the predictions of the accepted theory.

Arrhenius had already [107] observed that addition of weak acids to small concentrations of strong acids increased the velocity of inversion of cane sugar, on the average, 10 per cent per unit of concentration of weak acid. The small amount of the added acid which is dissociated is certainly not of this order. Besides this direct influence of the undissociated acid molecule, he also noticed that the increase in velocity is more than proportional to the hydrogen ion concentration with increasing concentration of catalyst acid. However, this is explained (see p. 134) in a different way from the results which we are now about to discuss. Again, in Abel's work [142, 117] on the catalysis of hydrogen peroxide by molybdic acid, the half dissociated permolybdic acid molecule (primary step) must be more efficient than the bivalent anion. It is true, however, that the completely undissociated acid seems to be ineffective in this case.

Meanwhile, more important observations, paving the way for a theory of catalysis by neutral molecules, are to be found in the work of Goldschmidt. He had already established (Goldschmidt and Sunde [133]) that the velocity of esterification in alcoholic solution increased more rapidly than the hydrogen ion concentration with increasing acid concentration, as Arrhenius had found for the inversion. In addition, the inhibitory effect of salts with common ions was less than would be expected according to the law of mass action, assuming catalysis by hydrogen ions only. Later,[134] it appeared that the self-esterification of trichloracetic acid (see p. 93) was accelerated about 10 per cent by its own sodium salt instead of being retarded. Goldschmidt had already considered the possibility of the action of complexes of neutral catalyst acid molecules, and certain anomalies in the catalytic efficiency of very weak acids, subsequently made the object of further investigation, also pointed to the existence of such complexes with alcohol.

First of all, the assumption that the undissociated catalyst acid, as well as the hydrogen ion, is a catalyst and is subject to an analogous inhibition

[142] E. Abel, *Z. Elektrochem.*, 18, 545 (1912).

by water, was treated mathematically. Here, the derivation is different from that given on p. 95, inasmuch as the gross catalyst concentration was then simply put equal to the hydrogen ion concentration, which is not permissible in the case of weak acids. In general, the following equilibria have to be taken into consideration:

1. The reactions in which C_2H_5OH and H_2O compete for the undissociated acid HAc.

$$\begin{array}{ccc} \mathrm{HAc} + \mathrm{C_2H_5OH} \rightleftarrows \mathrm{C_2H_5OH \cdot HAc}; \\ \zeta' \qquad b \qquad\qquad \xi' \end{array}$$

$$\xi' = K_1 \zeta' b,$$

and

$$\begin{array}{ccc} \mathrm{HAc} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3OAc}; \\ \zeta' \qquad n \qquad\qquad \eta' \end{array}$$

$$\eta' = K_3 \zeta' n.$$

2. The dissociation of the solvate so formed (hydroxonium or alcoxonium salt):

$$\begin{array}{ccc} \mathrm{C_2H_5OH \cdot HAc} \rightleftarrows \mathrm{C_2H_5OH \cdot H^{\cdot}} + \mathrm{Ac'}; \\ \xi' \qquad\qquad \xi \qquad\qquad \xi + \eta + \zeta \end{array}$$

$$\frac{\xi(\xi + \eta + \zeta)}{\xi'} = k_1$$

and

$$\begin{array}{ccc} \mathrm{H_3OAc} \rightleftarrows \mathrm{H_3O^{\cdot}} + \mathrm{Ac'}; \\ \eta' \qquad\qquad \eta \qquad\qquad \xi + n + \zeta \end{array}$$

$$\frac{\eta(\xi + \eta + \zeta)}{\eta'} = k_3$$

3. Finally the dissociation of the free acid:

$$\begin{array}{ccc} \mathrm{HAc} \rightleftarrows \mathrm{H^{\cdot}} + \mathrm{Ac'}; \\ \zeta' \qquad\qquad \zeta \qquad\qquad \xi + \eta + \zeta \end{array}$$

$$\frac{\zeta(\xi + \eta + \zeta)}{\zeta'} = k_2$$

By substituting K_1, in k_1 and K_3 in k_3, and combining the three equations for k_1, k_2, k_3, ξ is obtained as a function of ζ' (in the case of weak acids this is about equal to the analytical concentration of the catalyst c). Now the velocity of the reaction catalyzed by ions *and* by acid molecules must be:

$$\frac{dx}{dt} = (k\xi + k'\xi')(a - x),$$

and substituting for ξ and ξ', we obtain:

$$\frac{dx}{dt} = \left[\frac{kK_1k_1b\sqrt{\zeta'}}{\underbrace{\sqrt{K_1k_1b + k_2 + K_3k_3n}}_{\text{ions}}} + \underbrace{k'K_1b\,\zeta'}_{\text{molecules}} \right] (a - x).$$

According to this equation, the dependence of the first order " constants " upon the acid concentration (square brackets) must lie between 0.5 power and simple proportionality. This was actually found [133] and again in catalysis by trichlorbutyric acid.[136] A more important consequence of the theory, however, is that addition of electrolytes of the same anion (salts), diminishes only the first term in parenthesis by suppression of ionization, leaving a residual constant, corresponding to pure molecular catalysis.

This constant, which is quite incompatible with the idea of pure hydrogen ion catalysis, can actually be found by the addition of excess aniline salt of the acid. For example, the following values were obtained:

TABLE XI — RESIDUAL CATALYTIC ACTIVITIES OF UNDISSOCIATED ACIDS

Acetic acid	Butyric acid	Phenyl acetic acid	Formic acid
0.00075	0.00039	0.00054	0.011

Subtracting these from the total constants for the salt free acids, the first term in parenthesis, the constant for pure ion catalysis, is obtained:

TABLE XII — VELOCITY CONSTANTS FOR ION CATALYSIS

Acetic acid	Butyric acid	Phenyl acetic acid	Formic acid
0.0025	0 00105	0.00109	0.0458

In all cases, these values should be proportional to the square root of the acid concentration, which is at least nearly true. It is interesting also, that the purely molecular catalysis found when the salt is added, does not show any inhibition by water, because competition of water for the undissociated acid is unnoticeable, that is, the hydroxonium salt is almost completely dissociated.

Such residual velocities were found even in the case of picric acid,[143] al-

[143] H. Goldschmidt, *Z. Elektrochem.*, 17, 684 (1911).

though this acid is a strong acid in alcohol. Also, the ratio of the velocity in 0.1 N solution to that in 0.01 N solution was 4.63, while the ratio of the hydrogen ion concentrations obtained from the conductivities was 3.5. If, however, the residual constant, multiplied by the undissociated fraction of the acid, is subtracted from the velocity, a ratio of 3.55 is obtained for the pure ionic catalysis, in complete agreement with the results.

The ratio of the ionic constant to the molecular constant varies from acid to acid and also with the solvent. Further reference will be made to this point later, however (pp. 107 and 128).

As in the case of hydrogen ion catalysis, the most practical confirmation of Goldschmidt's esterification results was provided by the diazoacetic ester reaction. Braune [144] (see also Bredig) [141] investigated the effect of addition of salts of the same anion, when acetic acid, trinitrobenzoic acid, sulphosalicylic acid, trichlorbutyric acid and picric acid were the catalysts, and ethyl or methyl diazoacetic ester the substrate. He found that, although the dilution law is valid for the acids, the constant is not reduced to zero but to a residual constant independent of water, and, secondly, the catalysis with the acids alone increases more rapidly than the hydrogen ion concentration. (When c varies as $1 : 4$, k alters by $1 : 2.4$, while the expected variation with c is $1 : 2$.) Both of these results are rendered intelligible by the Goldschmidt equation on p. 103. The disagreement remaining in the data given in Fig. 13, already corrected for the degree of dissociation, is now quantitatively removed.[141] A point still outstanding (see p. 100) is that the pure ion catalysis always increases a little more rapidly than $\sqrt{c}$, showing that a further correction of the simple Ostwald theory is necessary.

The experiments of A. Hantzsch [145] confirming the general efficiency of undissociated acids merit some discussion at this point. Starting from optical observations, he came to the conclusion that the catalytic strength of an acid is not entirely measured by its hydrogen ion concentration, but, especially in homogeneous acid or indifferent solvents, the acid molecule itself is the effective agent. Thus, he extended the Ostwald measurements to higher concentrations and obtained the figures shown in the accompanying table. Here, n is the normality of the acid, k/n the velocity constant per equivalent of acid, of the specific efficiency. From the fact that this rises with the acid concentration instead of decreasing with the diminishing ion concentration per equivalent, Hantzsch assumed catalysis by the un-

[144] H. Braune, *Z. physik. Chem.*, **85**, 170 (1913).

[145] A. Hantzsch, *Ber.*, **58**, 612 (1925). [See, however, J. Brönsted and R. Bell, *J. Am. Chem. Soc.*, **53**, 2496 (1931).]

TABLE XIII — RATIOS OF VELOCITY TO NORMALITY FOR STRONG ACIDS

n	k/n for HCl	k/n for HBr	
0.01	0.00313	0.00318	Ostwald
0.1	0.00334	0.00341	Ostwald
0.5	0.00434	0.00447	Ostwald
1	0.00573	0.00683	Hantzsch
2	0.00895	0.01175	Hantzsch
4	0.0245	0.0410	Hantzsch

dissociated molecules of the acid. We shall see later (p. 133) however, that such conclusions are scarcely permissible in more than 1n aqueous solutions of electrolytes. Meanwhile, the specific difference between HCl and HBr, which comes out at high concentrations is worthy of note. Hantzsch made similar observations on the catalysis of the hydrolysis of diazoacetic ester in aqueous solution as shown in the accompanying table. The explanation

TABLE XIV — RATIOS OF VELOCITY TO ACID CONCENTRATION (HANTZSCH)

n	k/n for HCl	k/n for HBr
0.01	2	—
0.02	2	2.7
0.1	3.2	3.7

of these results must be deferred until the difficulties which arise have been discussed. In the meantime, much information is to be gained from the measurements of the action of acids on diazoacetic ester in nonaqueous and nonalcoholic media. Under these conditions, the reaction is no longer concerned with catalysis of hydrolysis or alcoholysis, but involves either the addition of acid (suppressed in alcoholic media) according to:

$$\begin{array}{l} H-C-COO\cdot C_2H_5 \\ \quad\diagup\diagdown \\ \quad N=N \end{array} + HX = \begin{array}{l} H-C-COO\cdot C_2H_5 \\ \quad\diagup\diagdown \\ \quad H\ \ X \end{array} + N_2,$$

or the catalytic formation of fumaric acid according to:

$$2\begin{array}{l} H-C-COO\cdot C_2H_5 \\ \quad\diagup\diagdown \\ \quad N=N \end{array} \xrightarrow{HX} C_2H_5\cdot OOC-\overset{H}{\dot{C}}=\overset{H}{\dot{C}}-COO\cdot C_2H_5 + 2N_2$$

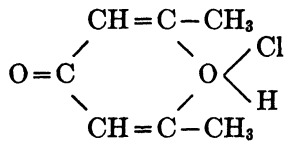
However, if it is assumed that the same acid-substrate intermediate is involved in all these cases, the constants of the nitrogen evolution may very

well be compared with one another. The following results which, owing to the extremely high velocity, are not very exact, were obtained:

TABLE XV — RATIOS OF VELOCITY TO ACID CONCENTRATION

In tetrachlorethane			In toluene	
n	k/n for HCl	k/n for HBr	n	k/n for HCl
0.01	160	250	0.01	2.2
0.02	150	300	0.02	14
0.1	120	—	0.1	27

The velocity in the indifferent tetrachlorethane is not only much greater than in water or toluene, but it is also independent of the concentration (referred to equivalent of acid). In this case then, only the undissociated acid can be effective. The velocity in toluene is similar to that obtaining in water, and, since a toluene compound of hydrogen chloride is known, it is assumed that toluene reduces the acid concentration by formation of such a compound in the same way that water does by hydroxonium salt or ion formation. Similarly, in the case of 2 : 6 dimethyl pyrone, which forms the pyronium salt



the reaction velocity in chloroform is only 1/700th of the velocity in tetrachlorethane. More recent experiments by Weissberger and Högen [145a] on the reaction between trichloracetic acid and diazoacetic ester in hydrocarbon solvents, show that the reaction velocity is diminished by the addition of ethyl ether, acetone and other substances which reduce the concentration of the acid by the formation of compounds.

The results of Arrhenius, Goldschmidt, and Bredig and co-workers indicating an effect of both hydrogen ion and acid molecule, were summed up by Snethlage,[146] a pupil of Bredig. By measurements on the picric acid catalysis of diazoacetic ester he established that the decreasing constants with increasing addition of salt (or base) all fell on a common curve; the constants diminished with increasing additions until a final residual constant

[145a] A. Weissberger and J. Högen, *Z. physik. Chem.*, **156**, 321 (1931).

[146] H. S. Snethlage, *Z. physik. Chem.*, **85**, 211 (1913); *Z. Elektrochem.*, **18**, 539 (1912).

was reached which did not change with further additions. These observations were found for all kinds of amine-bases. The theoretical equation for this curve is:

$$k = [k_H \alpha + k_m(1 - \alpha)] \cdot C_{acid},$$

where k_H is the velocity constant of hydrogen ion catalysis and k_m that of the undissociated molecule (residual constant). Snethlage now collected all the cases in which α was known from conductivity measurements, and calculated k_H and k_m. These are: esterification of ethyl alcohol and methyl alcohol by Goldschmidt; alcoholysis of diazoacetic ester in ethyl alcohol by Braune [144] and Snethlage [146]; inversion of sugar in water by Arrhenius [107] and Spohr.[147]

In this way, he found, for the first time, the important general relationship between the dissociation-equilibrium constant (affinity constant) and the ratio $k_m : k_H$. A selection from his calculations is given in the following table:

TABLE XVI

RELATION BETWEEN CATALYTIC RATIO, $k_m : k_H$ AND DISSOCIATION CONSTANT

Reaction	Catalyst	Diss. Const.	$k_m : k_H$	Solvent
Diazomethyl ester.....	Picric acid	5.7×10^{-4}	0.1	Ethyl alcohol
Diazoethyl ester.....	Picric acid	5.7×10^{-4}	0.06	Ethyl alcohol
Esterification.....	Picric acid	5.7×10^{-4}	0.04	Ethyl alcohol
Diazoethyl ester	Trichloracetic acid	4.5×10^{-6}	0.0018	Ethyl alcohol
Diazoethyl ester	Trinitrobenzoic acid	2×10^{-6}	0 0012	Ethyl alcohol
Inversion.....	Succinic acid	7×10^{-5}	0 01	Water
Inversion.....	Acetic acid	1.8×10^{-5}	0 006	Water
Inversion.....	Butyric acid	$1 5 \times 10^{-5}$	0.003	Water

Although there is considerable variation in the separate velocity constants of different reactions in different solvents, yet, in the same solvent, for the same acid, the ratio appears to be nearly independent of the reaction being catalyzed, and, from acid to acid and solvent to solvent, in all cases, is determined only by a single quantity, namely the dissociation constant of the acid in the particular solvent. We may, therefore, enunciate the proposition, that: the stronger an acid in the classical sense, the more efficient the undissociated molecule as catalyst.

For the strongest acids, not represented in the table, such as hydrochloric acid and nitric acid in water, or sulphosalicylic acid in alcohol, the ratio

[147] J. Spohr, *Z. physik. Chem.*, 2, 194 (1888).

$k_m : k_H$ increases to 1–2. (It is now known that the ratio $k_m : k_H$ can assume much greater values for strong acids, cf. Dawson and Millet, below)

A new reaction, namely, the enolization of acetone:

$$H_3C-CO-CH_3 \rightarrow H_2C=COH \cdot CH_3,$$

was added by Dawson and Powis.[148] It can be followed kinetically as the velocity determining process, since the enol form is taken up in a very rapid successive reaction with iodine before it can undergo the reverse reaction. Since hydrogen iodide is thereby formed, which is itself an acid catalyst, the velocity constant has to be extrapolated to zero time. The reaction is zero order with respect to acetone as long as acetone is used in considerable excess. The constant so obtained can be excellently represented, for all concentrations of added acids, by Snethlage's theory, which Dawson very aptly termed the "Dual Theory" of catalysis. They give the following values:

TABLE XVII

RELATION BETWEEN CATALYTIC RATIOS AND DISSOCIATION CONSTANT

Catalyst	k_m	k_H	k_m (corr.)	$k_m : k_H$	Diss. const.
Hydrochloric acid	811	437	780	1.77	5.1×10^{-2}
Dichloracetic acid	203	445	220	0.50	5.1×10^{-2}
β-Dibrompropionic acid	74	440	67	0.152	0.67×10^{-2}
Chloracetic acid	23.7	448	24.5	0.055	0.155×10^{-2}
Acetic acid	1.55	425	1.5	0.0034	0.0018×10^{-2}
	Mean =	440			

Under k_m (corr.) the figures calculated from the mean value $k_H = 440$ are given. Here, clearly, there is the same relationship with acid strength that Snethlage obtained. This is also shown in the comparison with the ratio $k_m : k_H$ of other reactions, made by Dawson and Powis:

TABLE XVIII — CATALYTIC RATIOS FOR VARIOUS REACTIONS

Catalyst	Sugar Inversion (Arrhenius [107]) (Palmaer) (Snethlage [146])	Ester hydrolysis (H. S. Taylor [150])	Enolization (Dawson [148])
Hydrochloric acid	2	2 to 3	1.77
Dichloracetic acid	—	0.02 to 0.16	0.5
Acetic acid	0.006	—	0.0034

[148] H. M. Dawson and F. Powis, *J. Chem. Soc.*, **103**, 2135 (1913).

It is evident here, as previously, that the ratio of the constants is determined only by the dissociation constant. Consequently, there must be a universal functional connection between these quantities. In an endeavor to get to the root of the problem, H. S. Taylor [150] plotted the logarithms of these quantities.[149, 150]

Besides the measurements already discussed, additional measurements of ester hydrolysis in water, in the presence of acids,[151] which could likewise be represented by the dual theory were included in the figure. This diagram is reproduced in Fig. 14. In spite of considerable individual fluctuations, the logarithms (negative since logarithms of real fractions) are very distinctly grouped around a straight line, whose angle of inclination is about 26°, corresponding to a tangent of 0.5. Since the line passes through the origin, the equation is:

$$\frac{k_m}{k_H} = K^{0.5}.$$

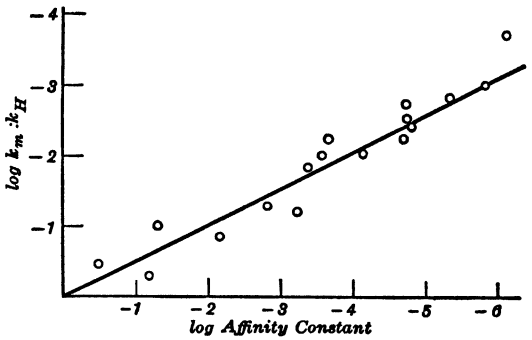


FIG. 14. Relation between the Catalytic Activity of the Undissociated Molecule and Acid Strength (H. S. Taylor).

We will come across a generalized form of this equation later (p. 128), when its general significance will appear. Taylor also discussed [149] the temperature independence of this relation. The account of the development of the dual theory will be briefly interrupted here, in order to mention two investigations that have led to the same conclusion more or less independently.

Blanksma [152, 153] had found that the reaction (see p. 136):

$$H_3C-CO-\underset{\dot{Cl}}{N}-C_6H_5 + HCl \rightarrow H_3C-CO-\underset{H\ \dot{Cl}}{\overset{Cl}{\dot{N}}}-C_6H_5$$

$$\rightarrow H_3C-CO-\underset{\dot{H}}{N}-C_6H_4Cl\ (p) + HCl$$

[149] H. S. Taylor, *J. Am. Chem. Soc.*, **37**, 551 (1915).
[150] H. S. Taylor, *Z. Elektrochem.*, **20**, 201 (1914).
[151] H. S. Taylor, *Medd. Nobel-Inst.*, **2**, 34–37 (1913).
[152] J. Blanksma, *Rec. Trav. Chim.*, **21**, 366 (1902).
[153] J. Blanksma, *Rec. Trav. Chim.*, **22**, 290 (1903).

the hydrogen-chlorine interchange catalyzed by hydrochloric acid, is first order with respect to the amide, and second order with respect to the hydrochloric acid. The assumption that the intermediate step is an ammonium salt was confirmed by Acree [154] from the following reactions:

$$\begin{array}{l} H_3C-CO-NCl-C_6H_5 + HBr \searrow \qquad\qquad Br \\ \qquad\qquad\qquad\qquad\qquad\quad H_3C-CO-N\ C_6H_5 \\ H_3C-CO-NBr\ C_6H_5 + HCl \nearrow \qquad\quad H\ Cl \end{array}$$

$$\rightarrow H_3C-CO-NH-C_6H_4Br + HCl$$

in which the formation of the same end product may be thus readily explained. It is important to note that the above reactions also proceed in proportion to the square of the acid concentration, and that the HBr reaction is 1000 times faster than the HCl reaction. Sulphuric acid and acetic acid catalyze in the same way, but with quite characteristic velocities. All these facts are clearly incompatible with catalysis by hydrogen ions.

The question of the formation of an intermediary ammonium ion:

$$H_3C-CO-\overset{+}{\underset{HCl}{N}}\cdot\cdot\cdot C_6H_5,$$

does not arise, as its concentration would clearly depend on the first power of the concentration of strong acids. On the other hand, the undissociated ammonium salt, as it is written above, would be proportional to the concentration of the hydrogen ions [167] and to the anions, and, consequently, to the square of the acid concentration. These considerations led Acree, as early as 1907, to postulate catalysis by undissociated acid molecules. Such a thing was contrary to the prevailing notion of the favored position of ions, and in 1913,[155] when the dual theory was in process of formation in Europe, he connected the effect, in very modern fashion, with the dipole nature of such salt-like molecules. At the same time, he suggested a simple explanation of Arrhenius's equation [107] for the action of acids in the inversion process:

$$k = ac + bc^2 \text{ } (c \text{ is the acid concentration})$$

by assigning the square term to the undissociated molecules of acid. For strong acids, whose conductivity does not obey the dilution law, he introduced empirically, instead, the degree of dissociation obtained from the conductivity at each concentration, in the form:

$$k = [a'\alpha + b'(1 - \alpha)]\, c.$$

[154] S. F. Acree and J. M. Johnson, *Am. Chem. J.*, **37**, 410 (1907).
[155] S. F. Acree, *Amer. Chem. J.*, **49**, 345 (1913).

In this way, he was able to recalculate the experiments of Arrhenius and Ostwald [124, 125] successfully. He also came to the conclusion that the effect of the undissociated part is greatest in the case of strong acids. It is interesting that the same result was obtained with respect to molecules of base, in the catalysis by bases of Koelichen's condensation of acetone to diacetone alcohol. We shall find, however, that this conclusion is difficult to establish owing to a physical factor not taken into consideration.

The decomposition of optically active camphoric acids was also interpreted by Bredig and Fajans [156] and Fajans [156] as a catalysis by undissociated molecules of base. We have already discussed the optical specificity of these reactions (p. 84). The reaction occurs in basic solvents like aniline or nicotine, and only takes place in other solvents like acetophenone or nitrobenzene when such bases are dissolved in them. Since ions can hardly be involved in these circumstances, the undissociated salts formed by reaction with the undissociated base molecules are supposed to be Arrhenius intermediates.

We will now take up the further development of the dual theory, with which Dawson is particularly identified. First of all in collaboration with Reimann,[157] the 'residual constants' obtained by Snethlage and Braune, as well as by Goldschmidt, by addition of salts with an anion in common with the catalyst acid, were also found for the enolization of acetone. Making certain assumptions, the constants $k_H = 482$ and $k_m = 21$ were derived from catalysis and conductivity of pure chloracetic acid, and experiments on the addition of as much as $0.2n$, sodium salt, to $0.05n$ and $0.1n$ acid could be quantitatively reproduced on the basis of these values. Later unpublished experiments (see ref.[158]) showed, however, that the decrease in velocity previously observed with salt addition passes through a *minimum* with larger additions of salt, and becomes a straight line *rising* with the salt concentration. "This is illustrated in Fig. 14*a*, which shows the curve expected on the basis of pure hydrogen ion catalysis, that predicted by the dual theory, and the curve found experimentally."

Since this result is clearly incompatible with the dual theory, it became necessary to ascribe a catalytic effect to the anion of the acid, noticeable at higher salt concentrations. Dawson has himself [158] given a review of the work (in collaboration with Carter, Key, Dean, Lowson, and Hoskins), which led to this extension of the theory, and this will be followed here.

[156] G. Bredig and K. Fajans, *Ber.*, **41**, 752 (1908); K. Fajans, *Z. physik. Chem.*, **73**, 25 (1910).

[157] H. M. Dawson and C. K. Reimann, *J. Chem. Soc.*, **107**, 1426 (1915).

[158] H. M. Dawson, *Trans. Faraday Soc.*, **24**, 642 (1928).

Three methods are described for the determination of the constants of the three catalysts now postulated. The first depends on the variation of salt concentration y, at constant acid concentration c, which is the only

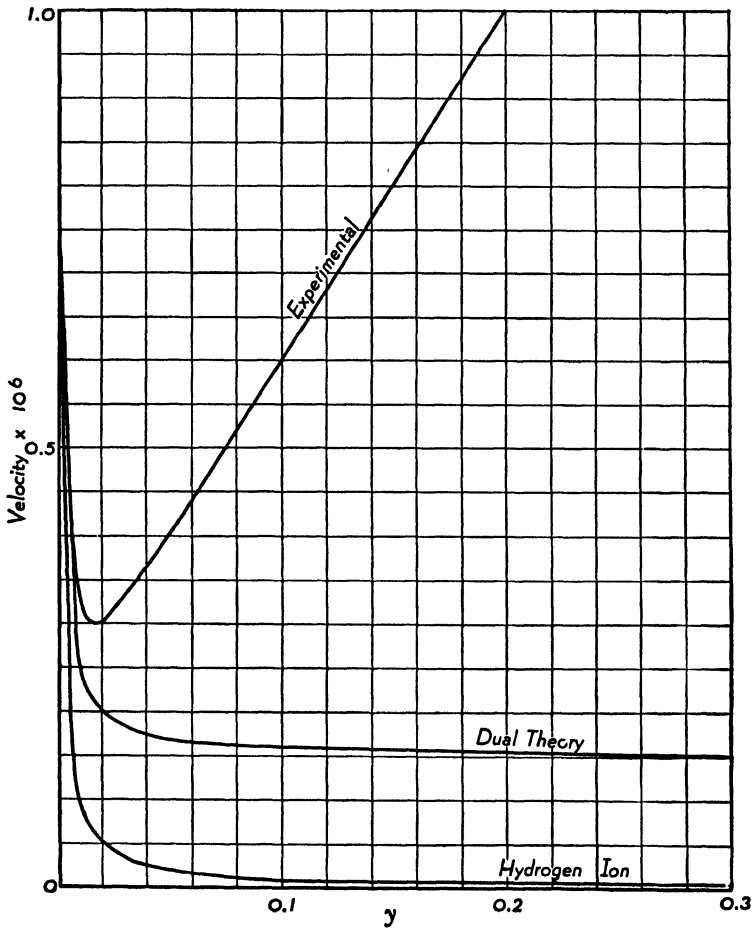


FIG. 14*a*. Catalysis of the Acetone-Iodine Reaction, with the Catalyst: 0.1n CH_3COOH + y n CH_3COONa (Dawson).

method which has so far been considered. The fundamental equation for the combined catalysis is:

$$\frac{dx}{dt} = v = k_H(H^\cdot) + k_a(Ac') + k_m(HAc)$$

For weak acids and large y we may write:

$$v = k_{\mathrm{H}} \cdot \frac{Kc}{y} + k_a - y + k_m \cdot c$$

On the other side of the minimum, where the curve rises linearly (but approaches the residual constant asympotically in the case of dual catalysis only), the first term, referring to the hydrogen ion, may be neglected, and k_a, the anion constant, is given by the slope. The linear portion, extrapolated backwards, intersects the v axis in $v = k_m c$. In this way, the values $k_a = 4 \times 10^{-6}$ and $k_m = 1.5 \times 10^{-6}$ were determined for enolization by acetic acid, while $k_{\mathrm{H}} = 4.65 \times 10^{-4}$ was obtained from dilute hydrochloric acid.

The second method is that of isohydric solutions, that is, solutions with constant $c/y = q$, obtained by dilution of a given mixture. In this case,

$$v = v_o + (k_a + qk_m)y,$$

where v_o is the velocity at infinite dilution. The v-y curve is a straight line whose slope gives the sum of two quantities, from which the values of k_a and k_m can be obtained by another series of measurements with different q. The values are in good agreement with those obtained by the first method.

In the third method, which was at first used by all authors for the determination of k_{H} and k_m, the constants are determined from the concentration relations of the velocity in pure salt-free acids. In these circumstances:

$$[\mathrm{H}^{\cdot}] = [\mathrm{Ac}'] \quad \text{and} \quad [\mathrm{HAc}] = c - [\mathrm{H}^{\cdot}],$$

and it follows that,

$$v = (k_{\mathrm{H}} + k_a - k_m)\,[\mathrm{H}^{\cdot}] + k_m \cdot c.$$

For very weak acids, we can put

$$[\mathrm{H}^{\cdot}] = \sqrt{Kc},$$

and hence,

$$\frac{v}{\sqrt{c}} = (k_{\mathrm{H}} + k_a - k_m)\sqrt{K} + k_m \sqrt{c}.$$

The reduced velocity $v/\sqrt{c}$ is then a linear function of $\sqrt{c}$ (not the velocity itself, in agreement with Goldschmidt and Braune). k_m is given by the slope. When k_{H} is known and k_a is known or very small, the dissociation constant K can be obtained from the intercept on the ordinate axis. The value of k_m given by this method actually agrees with those derived

by the other methods and even coincides with the Ostwald conductivity measurements. For stronger acids, in which the dissociated part cannot be neglected, Dawson determined k_m and K in this way, only as a first approximation, and calculated α, the degree of dissociation from K. Then:

$$[H^{\cdot}] = \sqrt{Kc(1-\alpha)},$$

and the equation:

$$\frac{v}{\sqrt{c(1-\alpha)}} = (k_H + k_a - k_m)\sqrt{K} + k_m\sqrt{c(1-\alpha)},$$

was similarly evaluated. This procedure can be repeated and very good values obtained in the second approximation. For example, glycollic acid gives as a first approximation, $K = 1.38 \times 10^{-4}$; as a second approximation, 1.50×10^{-4}, identical with Ostwald's value.

The Catalytic Catenary: From the relations:

$$[Ac'] = \frac{K[c - [H^{\cdot}]\,]}{[H^{\cdot}]} \quad \text{and} \quad [HAc] = c - [H^{\cdot}],$$

the velocity follows as a function of the hydrogen ion concentration:

$$v = (k_H - k_m)\,[H^{\cdot}] + \frac{k_a Kc}{[H^{\cdot}]} - k_m c - k_a K.$$

Introducing $p_H = -\log [H^{\cdot}]$, the expression becomes:

$$v = (k_H - k_m) \cdot 10^{-p_H} + k_a Kc \cdot 10^{p_H} - k_a K.$$

This is the equation of a catenary with a minimum in the plot, v against p_H, at:

$$p_H = -\log \sqrt{\frac{k_a Kc}{(k_H - k_m)}}$$

It can be shown that, at this point, the " isocatalytic point," catalysis by hydrogen ions and by anions is equal, and, further, that the whole velocity curve is symmetrical about this point in relation to $\log [H^{\cdot}]$ or p_H. We shall see later that this curve is very important in the special case that $[OH']$ is the effective anion (see Fig. 15, p. 118). Dawson's results are in close agreement with these requirements over a wide range.

As the whole conception is bound up with the new ideas on solutions of electrolytes, it will again be discussed in another place (see p. 149).

Finally, mention will be made of another reaction to which the extended dual theory has been successfully applied, namely the mutarotation of

glucose, kinetically studied by Lowry and Smith.[159] This reaction, which has become a very valuable example in the subsequent development of solution catalysis, will be considered in detail later. However, there are some points rather outside the scope of the next section, which have to be considered in connection with the dual theory.

Lowry and Smith established that, with hydrochloric acid concentration above $0.4n$, the velocity of mutarotation increases more rapidly than the acid concentration. This can be attributed to the action of undissociated acid molecules, giving $k_m : k_H = 1.5$, in good agreement with the other reactions (see p. 108). More exact results, which can be obtained in the case of the weaker acetic acid give $k_m : k_H = 0.018$, which is rather too high. A strong anion catalysis is indicated in this reaction by a marked linear increase with the concentration of the added acetate, from which it follows that $k_a = 0.07$; the ratio to k_H is similar to that obtaining in the enolization. It is interesting in regard to what follows, that ammonium ions, as well as undissociated ammonia, in ammonium acetate, catalyze the reaction. The effect of the salt is greater than the sum of the calculated effects (apparent promotion: see p. 88) owing to hydrolysis taking place. As regards the anion catalysis, it is interesting to note that there appears to be a similar connection with the classical acid strength, as with neutral molecules; for example, phenol ions have a perceptible effect but chloride ions none at all.

In the foregoing, we have traced the manner in which the consideration of various deviations from the old idea of pure $H^{\cdot}$ and OH' ion catalysis has finally led to a theory which allows of a far wider dissemination of catalytic powers. This signifies a considerable advance, especially as the theory had to contend with deep-rooted prejudices regarding the exclusive reactivity of ions. So far, we have developed the dual theory as it was originally enunciated, on the basis of the classical theory of dissociation. Naturally, it has met with many attacks on this account and has been modified in diverse special forms. However, not all effects can be criticized in this way, especially those associated with weak acids, which formed the standard catalysts of the theory. In the following sections, we shall see that the knowledge of the chemical multiplicity of catalysts, afforded by the dual theory, extends still further, and eventually paves the way towards an insight into the inner chemistry of catalysis in solution.

The Theory of Interacting Ions: Before continuing with the logical development of this aspect of the subject, we must consider a theory originally derived from the opposite point of view, known as the theory of " inter-

[159] T. M. Lowry and G. F. Smith, *J. Chem. Soc.*, **129**, 2539 (1927).

acting ions." In its modern form, however, it is not very far removed from the conception which we have so far developed, and formally approaches it very closely. Its merit is chiefly that of having included, and kinetically formulated, a whole complex of phenomena, subsequently of great importance, and therefore it must be considered here.

The so-called " theory of interacting ions," was developed chiefly by H. von Euler and originated in the notion of the exceptional reactivity of ions, which prevailed before the discovery of the phenomena of dual catalysis. It follows similar lines to the explanation which Bredig had given for the reaction between hydrogen peroxide and iodide ions (Brode [118]). This process, of course, may be divided into two parts, one catalyzed by hydrogen ions:

$$\frac{dx_1}{dt} = k \cdot [H_2O_2]\,[H^\cdot]\,[I'],$$

and the other uncatalyzed. The latter may likewise be conceived as a catalyzed reaction, involving an interacting anion of the acid hydrogen peroxide:

$$\frac{dx_2}{dt} = k'[HO'_2]\,[H^\cdot]\,[I'],$$

and, since

$$[HO'_2] = \frac{K[H_2O_2]}{[H^\cdot]},$$

the hydrogen ion concentration cancels out, in agreement with the observations.

Similarly, Euler [160] adopted the view that, in general, the reaction intermediates are ions of the substrate considered as a weak electrolyte, and that the catalyst — hydrogen ions, hydroxyl ions, or salts — only increase the concentration of these intermediates and consequently increase the " mobility " of the system. The formation of a salt between catalyst and substrate is an intermediate step in this process. For example, according to the original formulation, in the hydrolysis of acetic ester, acetyl chloride and ethyl chloride are formed first of all and then rapidly dissociate, giving acetyl and ethyl cations. The temperature coefficient is given by the heats of dissociation of the substrates; in the inversion of cane sugar, by the heats of dissociation of sugar and water.[161]

The theory, in its original form, was criticized by Wegscheider,[162] and

[160] H. v. Euler, *Z. physik. Chem.*, **32**, 348 (1900).
[161] H. v. Euler, *Z. physik. Chem.*, **36**, 641 (1901); *Ber.*, **33**, 3202 (1900).
[162] R. Wegscheider, *Z. physik. Chem.*, **39**, 257 (1902); **41**, 62 (1902).

was afterwards restated by Euler.[163] This later form especially states that the stable concentration of substrate ions is dependent on the catalyst concentration, and that the velocity is determined by the rate at which these ions react. The theory has been used in a large number of subsequent investigations (e.g.[164]) of acid and base catalysis of inversion and mutarotation. Sucrose is supposed to be an amphoteric weak electrolyte, dissociating as follows:

$$Z + H_2O \rightleftarrows ZH^{\cdot} + OH' \text{ with diss. const. } K_b$$

and

$$Z + H_2O \rightleftarrows ZOH' + H^{\cdot} \text{ with diss. const. } K_a.$$

The degree of dissociation (dissociated part divided by the total sugar) is then:

$$\frac{[ZH^{\cdot}]}{[ZH^{\cdot}] + Z} = \frac{K_b}{K_b + [OH']},$$

and

$$\frac{[ZOH']}{[ZOH'] + Z} = \frac{K_a}{K_a + [H^{\cdot}]}$$

If we now let K_w represent the dissociation constant of water, k_u the velocity of reaction of sucrose molecules (dipolar ions or Zwitterions), and if, in addition, the specific reactivities of the ions are equal and, in the system of measurement used, are equal to one, the velocity constant becomes:

$$k\left(1 + \frac{K_b}{K_b + \frac{K_w}{[H^{\cdot}]}} + \frac{K_a}{K_a + [H^{\cdot}]}\right) = k_u + \frac{K_b}{K_b + \frac{K_w}{[H^{\cdot}]}} + \frac{K_a}{K_a + [H^{\cdot}]},$$

or approximately:

$$k = k_u + \frac{K_b}{K_w}[H^{\cdot}] + \frac{K_a}{[H^{\cdot}]}.$$

It is evident that this equation leads to catenaries quite analogous to those obtained by Dawson (see p. 114) for catalysis by acid ions and molecules. The relationship between the constants k for the hydrolysis of benzamide and ethyl acetate and p_H, is illustrated in Fig. 15 according to the results of Euler and Ölander.[164]

According to Ölander,[165] a similar minimum also appears in the saponification of esters and sulphonic acid esters. The minimum is raised above the p_H axis owing to the fact that the uncatalyzed reaction has a definite

[163] H. v. Euler, *Z. physik. Chem.*, **40**, 498 (1902).
[164] H. v. Euler and A. Ölander, *Z. physik. Chem.*, **131**, 107 (1927).
[165] A. Ölander, *Z. physik. Chem.*, **129**, 3 (1927).

velocity k_w. The exact minimum or " isocatalytic point " is at:

$$p_{H_i} = \sqrt{\frac{K_a K_w}{K_b}},$$

when both kinds of ions are assumed to have equal reactivities. Thus, knowing the constant K_a for dextrose and its stability maximum (isocatalytic point) the basic constant K_b was found to be 10^{-19} (Euler and Hedelius),[165a] and using this number, the sucrose catenary could be satisfactorily represented. Euler hopes, therefore, in this way to be able to predict both catalysts and catalytic velocities.

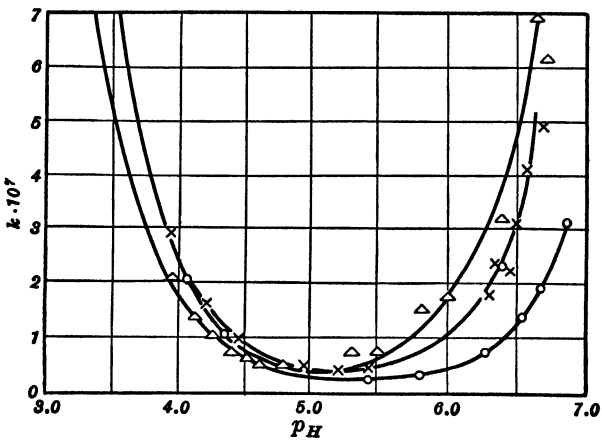


FIG. 15. Catenary Dependence of Rate of Hydrolysis on p_H (v. Euler and Ölander).

This treatment of mutarotation and inversion was corroborated and extended in a detailed investigation by Kuhn and Jakob.[166] They concluded that the p_H curve for inversion is asymmetric about the isocatalytic point, and ascribed a specific reactivity to the anion 2.1 times that of the cation. The isocatalytic point now no longer coincides with the isoelectric point, in accordance with the above equation, but is given by:

$$p_{H_i} = \sqrt{\frac{K_a}{K_b} \cdot K_w \cdot \frac{k_a}{k_b}},$$

where k refers to the specific reactivity of the ions. Making this correction,

[165a] H. v. Euler and A. Hedelius, *Biochem. Zeit.* 107, 150 (1920).
[166] R. Kuhn and P. Jakob, *Z. physik. Chem.*, 113, 389 (1924).

the value $K_b = 7.8\ 10^{-17}$, considerably greater than the previous value, was obtained from the isocatalytic point.

It is to be particularly noted that, so far, we have only dealt with the application of the theory, and that there has been no actual proof of the fundamental idea of the theory of interacting ions. This has been emphasized by Skrabal.[108] Among other things, he shows that the assumption of specific reactivities does not mean an asymmetry in the curve, as it only comes in as a factor and therefore the curve obtained when the logarithm of the velocity constant is plotted against p_H must *always* possess two branches symmetrically inclined 45° to the horizontal axis. Different values of the constants cause lateral displacement or variation of the breadth of the horizontal k_w portion, and the forms assumed by the curve with different ratios of the constants, as plotted by Skrabal, are shown in Fig. 16.

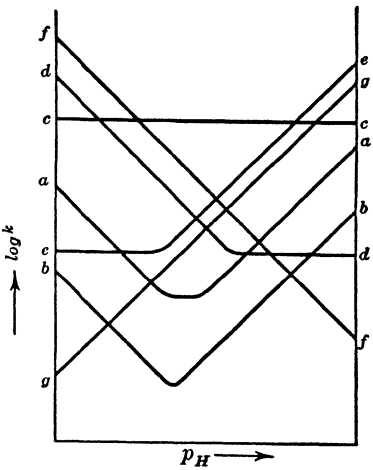


FIG. 16. Dependence of Rate of Hydrolysis on p_H for Various Ratios of the Individual Constants, Plotted Logarithmically (Skrabal).

The following reactions, for the most part due to Skrabal's investigations, have been classified according to one or other of the types illustrated.

Type	Reaction
c	Production of CO_2 from camphoric acid and acetoacetic acid,
b	Hydrolysis of acid amides and γ-lactones,
d	Orthoacetic ester → ethyl acetate,
	Orthocarbonic ester → ethyl carbonate,
e	Hydrolysis of β-lactones and esters of mineral acids,
g	Nitroso-triacetone amine → nitrogen + phorone,
	Diacetone alcohol → acetone,
	Various autoracemizations,
	Hydrolysis of ethyl carbonates,
f	Hydrolysis of diazoacetic ester,
	Creatine → creatinine,
	Hydrolysis of ethers,
	Inversion of sugars.

According to Skrabal, the catalytic constants of $H^{\cdot}$ and OH', for the specified exchange reactions of "organo acids" (alcohols A—OH, acids

R—O—H, esters R—O—A, anhydrides R—O—R, ethers A—O—A, water H—O—H) determined by the form of the curves, may be empirically arranged as uniform functions of the radicals A, R, and H.

This led Skrabal to the conclusion that the Euler theory is not a probable one, especially in view of the fact that the known dissociation constants frequently show a different constitutive variability to the velocity. In particular, he pointed out that the theory cannot be proved merely from the form of the catenary, as proportionality to [H˙] and [OH′] may be explained in other ways, e.g., by intermediate compounds.

In his view, the theory will first obtain confirmation when the curve is again found to become horizontal at extreme p_H values, owing to complete dissociation of the substrate. Recently, Euler [167] has actually observed a phenomenon of this sort in the hydrolysis of acetamide in the strong acid region, and, in the case of dioxy-piperazine, has even remarked the effect of two steps in the dissociation. However, Skrabal [106] is of the opinion that such evidence can only be obtained under conditions of concentration so extreme as to render the calculation uncertain (salt error).

From the fact already discussed [110a] that replacement of the hydrogen ion by deuterium reduces the velocity of mutarotation but accelerates the inversion of sugar, it is to be concluded that the Euler theory fails in the first case and is sustained in the second. Decisions as to the theory, are, therefore, only valid from reaction to reaction. (See also Hammil and LaMer.[167a])

It might very well be said, in summing up, that the experimental investigation of acid-base catalysis, which has been stimulated by the theory of interacting ions, has, almost without exception, led to quite unequivocal results, so much the more since the Kuhn-Jakob mutarotation formula has been confirmed by Lowry and Smith.[159] In regard to *explanation*, however, it cannot be claimed that the theory has been proved. The theory certainly agrees with the facts in all points, but, as we saw above, that is no proof of its correctness, and such proof will be hard to obtain. It can only be said with certainty that an uncatalyzed or water catalyzed reaction, an H˙ catalyzed reaction and an OH′ catalyzed reaction take place simultaneously, and conclusive information as to the composition of the intermediate formed thereby, cannot be derived from the kinetics alone, because of the innate ambiguity attaching to each proportionality factor (see p. 74).

In reality, however, the situation is not so complicated as it might appear

[167] H. v. Euler, *Trans. Faraday Soc.*, **24**, 651 (1928).

[167a] W. H. Hammil and V. K. LaMer, *J. Chem. Phys.*, **2**, 891 (1934).

from the above considerations, as it is almost indifferent from the chemical point of view, whether the primary reaction is:

$$Z + H^{\cdot} \rightarrow ZH^{\cdot} \qquad \text{(Brönsted [130])},$$

or $$Z + H^{\cdot} \rightleftarrows ZH^{\cdot} \qquad \text{(Bjerrum [109])},$$

or $$Z + H_2O \rightleftarrows ZH^{\cdot} + OH' \qquad \text{(Euler)}.$$

All these conceptions express the one significant fact that the H-nucleus of hydroxonium or of water, has a special efficiency in regard to the substrate concerned in the reaction, and, from this fact, we have been able to obtain a very fundamental view of homogeneous catalysis in solution, as we shall see in the next section.

The Proton Mechanism of Acid-Base Catalysis: During the last decade, a theory has been worked out and given experimental foundation by Lowry on the one hand, and Brönsted on the other, with the object of bringing the phenomena of catalysis in aqueous solution, so far as they concern acid-base catalysis, within a single uniform point of view. All the different standpoints from which the problem has so far been discussed, are apparently consistent with one another when considered from this new position.

Lowry's attention was first engaged in the study of mutarotation, the apparently spontaneous alteration in the rotation of optically active substances such as nitro-camphor or glucose derivatives. This involves the wandering of an H atom to another position and displacement of the bonds in the molecule; a kind of tautomerism or desmotropism for which Lowry [168] coined the name prototropy.

He found that these prototropic changes do not occur spontaneously, but actually come to a standstill in the absence of catalysts. Thus, the mutarotation of nitro-camphor in chloroform is completely stopped when the solvent contains traces of phosgene,[169] which prevents catalysis by removal of the basic impurities through the formation of carbamide. Furthermore, as evident from the work of Lowry and Richards,[98] Lowry and Faulkner,[98] and Lowry and Owen,[170] as reported by Lowry,[171] the mutarotation of the more soluble methylated and acetylated glucoses in chloroform, benzene, ethyl acetate, and pyridine, could be stopped by very careful purification, and especially by the exclusion of water. All these solvents, therefore, are not catalysts in themselves, while water is a " complete catalyst." A particularly noteworthy observation [98] is that pure, dry, pyridine and pure,

[168] T. M. Lowry, *J. Chem. Soc.*, **123**, 828 (1923).
[169] T. M. Lowry and E. H. Magson, *J. Chem. Soc.*, **93**, 119 (1908).
[170] T. M. Lowry and G. G. Owen, *Proc. Roy. Soc.*, A **118**, 505 (1928).
[171] T. M. Lowry, *Reunion Intern. de Chim. Phys.*, p. 219, Paris, (1928).

dry, cresol cannot produce mutarotation alone, but, mixed with water, or together, they effect a rapid change.

Lowry concludes from these facts, that neither indifferent solvents, nor acids and bases alone, catalyze mutarotation. In order to bring about reaction, it is necessary to have an amphoteric solvent such as water, or a combination of acid and base, or a combination of acid *or* base with water, the water functioning as base or acid.

Since this discovery also extends to nonaqueous solvents, acids and bases can no longer be defined according to the ideas of classical physical chemistry, as substances which furnish $H_3O^{\cdot}$ or OH' ions by dissociation. Therefore, as Brönsted [172, 173] has also pointed out, a new and broader definition has to be employed. According to this definition, *all molecules which are able to furnish a proton are called acids, and all molecules which can take up a proton are called bases.* Consequently, it is a matter of indifference whether the molecule is charged or neutral, and we have the general relation:

$$\text{acid} \rightleftarrows \text{base} + H^{\cdot}$$

A few examples will help to make this clear:

acid	$\rightleftarrows$ base	$+ H^{\cdot}$,
HSO_4'	$\rightleftarrows SO_4''$	$+ H^{\cdot}$,
CH_3COOH	$\rightleftarrows CH_3COO'$	$+ H^{\cdot}$,
OH_2	$\rightleftarrows OH'$	$+ H^{\cdot}$,
$OH_3^{\cdot}$	$\rightleftarrows OH_2$	$+ H^{\cdot}$,
$NH_4^{\cdot}$	$\rightleftarrows NH_3$	$+ H^{\cdot}$,
$[Co(NH_3)_5OH_2]^{\cdot\cdot\cdot}$	$\rightleftarrows [Co(NH_3)_5\ OH]^{\cdot\cdot}$	$+ H^{\cdot}$.

This definition obviously embraces the older definitions and goes beyond them. The hydroxonium (" hydrogen ") ions and hydroxyl ions assume a predominant rôle, only because of the fact that, in aqueous solution, their co-ordinated base or acid happens to be the solvent.

In water, which can act equally well as a " proton donor " (acid) or as a " proton acceptor " (base), prototropic reactions should therefore be catalyzed not only by acids and bases themselves, in combination with water, but also by *anions* and *cations*. According to the new conception, these are bases and acids respectively, so that anions of weak acids should be particularly effective. This directly corresponds to the results obtained by Dawson (see p. 111) and which he expressed in the extended theory of dual catalysis. Accordingly, as we shall see below,[111, 171] Lowry also classes the

[172] J. Brönsted, *Rec. Trav. Chim.*, **4**, 718 (1923).
[173] J. Brönsted, *J. Phys. Chem.*, **30**, 777 (1926).

enolization of ketones, which includes Dawson's typical example, among prototropic reactions.

Lowry's own experiments on the mutarotation of glucose in aqueous solution have confirmed and materially extended the dual theory. Lowry and Smith [159] found that hydroxonium and hydroxyl ions are not the only catalysts, but that water is itself effective at the same time, because of its amphoteric properties, as well as undissociated acid molecules which act as donors, and acid anions, which act as acceptors (bases). With regard to the latter, it is interesting to note that acetate ions are good catalysts, but chloride ions do not catalyze at all, because of their very small tendency to take up protons, hydrochloric acid being a highly dissociated acid. Furthermore, ammonium ions, which, from the point of view of the above definition, may be considered as acids, have about one-tenth of the catalytic efficiency of water. The following are the velocity constants which have been obtained for catalysts in molar concentrations.

TABLE XIX — VELOCITY CONSTANTS FOR MOLAR CONCENTRATIONS OF CATALYST

Acid	HCl (?)	0.54
	H_3O^+	0.36
	CH_3COOH	0.0065
	NH_4^+	0.0012
Amphoteric water		0.0147
Bases	OH'	8000 [174]
	CH_3COO'	0.069

Salts of weak acids and bases, such as ammonium acetate and pyridine phenolate, exert an effect greater than that calculated from the sum of the ionic effects, because an acid-base pair is formed by hydrolysis. Additional data regarding this reaction will be discussed in connection with Brönsted and Guggenheim's work (see p. 126) on the same problem.

How is this discovery of the necessity of the simultaneous presence of acids and bases in prototropic changes to be explained? Lowry [111, 171] has endeavored to supply an answer to the question on the basis of the electronic theory of homopolar valency, which has been elaborated during the last few years. Fundamentally, the change is supposed to consist in the wandering of a hydrogen atom and the displacement of a bond in the molecule. According to the new theory, the proton is removed from its original position by a " base " and given up at its new position by an " acid," and an electron wanders simultaneously, accompanied by an alteration of the binding in the interior of the molecule. Consequently, we may speak of

[174] T. M. Lowry and G. L. Wilson, *Trans. Faraday Soc.*, **24**, 683 (1928).

an "electrolytic theory of catalysis," whereby the molecules are electrolyzed between electrodes consisting of acid and base. By way of illustration, the process is reduced to a series of separate steps in the following example of ketization of an enol, although, on principle, Lowry would rather conceive them as occurring simultaneously.

Beginning with the enol:

$$H : O : \dot{C} : : \dot{C}$$

(only the valence electrons are represented, including those shared by the substituents omitted from the carbon atoms) a proton is first of all removed by a base, leaving an enol anion behind:

$$: \bar{O} : \dot{C} : : \dot{C} \quad + H^+.$$

This changes by electron shifts, into a hybrid ion with a semi-polar double bond:

$$: \bar{O} : \overset{+}{\dot{C}} : \cdot \cdot \dot{C}^- + H^+.$$

Another electron shift (always from left to right) between the O^- atom and the neighboring C-atom produces the ketone ion:

$$O : : \dot{C} : \dot{C}^- : \quad + H^+,$$

which finally takes up a proton from an acid and becomes a neutral ketone molecule:

$$O : : \dot{C} : \dot{C} : H.$$

The enolization process (see p. 108) is written in the reverse way.

Hydrolytic reactions, such as saponification and inversion, which also exhibit a catalytic catenary and acid-base catalysis in the old sense can be represented by a corresponding, though somewhat different mechanism:

In the ester: $H_3CCO : OC_2H_5$, the valence electron pair is completely incorporated in the ethoxyl when a proton is taken up from an acid, with the formation of an alcohol:

$$C_2H_5\bar{O} : + H^* = C_2H_5O : H,$$

while the acid residue, deprived of an electron, combines with the valence pair of a hydroxyl ion to form a molecule of acid:

$$H_3C\overset{+}{C}O + : OH = H_3CCOOH.$$

The characteristic difference between the two cases is that here the base (in the newer sense) can only be the hydroxyl ion. It is easy to understand therefore, why other bases and especially anions of acids, do not catalyze the reaction. There is no limitation with regard to the acid, however, and

indeed we have seen (p. 109) that undissociated acid molecules can readily take the place of the hydroxonium ion.

We have here, therefore, a good physical interpretation of the results of the dual theory. The basic ideas of the theory of interacting ions may also be detected, in rather altered form, in the consideration of intermediary ions in ketization. The only difference is [171] that the substrate ions postulated by Euler are not actually in equilibrium (Arrhenius intermediate), but that their formation and removal in the " electrolysis " takes place as one event. In this way, the second, exothermic process provides the energy for the first strongly endothermic process, the catalysis of which now becomes intelligible from an energy point of view. According to Lowry, then, the ions are, at best, quite short lived van't Hoff intermediates.

The problem has been worked out mathematically by Skrabal [106] according to the kinetic characteristics of the intermediate in prototropic catalysis. In acid catalysis, for example, the fundamental reaction scheme runs as follows:

$$S + H^{\bullet} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z_1 \ (Z_1 = \text{cation}),$$

$$Z_1 + M \underset{k_4}{\overset{k_3}{\rightleftarrows}} Z_2 + H^{\bullet} \ (M = \text{water}),$$

$$Z_2 \xrightarrow{k_5} B + M.$$

In the same way, as on p. 74, it can readily be deduced that the equation:

$$\frac{d[B]}{dt} = k[S]\,[C]$$

found experimentally with constant, excess [M], only results when Z_1 is a van't Hoff intermediate, or when Z_1 is an Arrhenius and Z_2 a van't Hoff intermediate, but not when both intermediates are in equilibrium.

The corresponding scheme for the "uncatalyzed reaction," i.e. the reaction catalyzed through the amphoteric properties of water, is on the other hand:

$$S + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z_1 + OH' \ (Z_1 = \text{cation}),$$

$$Z_1 + H_2O \underset{k_4}{\overset{k_3}{\rightleftarrows}} Z_2 + H^{\bullet},$$

$$Z_2 \xrightarrow{k_5} B,$$

$$H^{\bullet} + OH' \overset{K_w}{\rightleftarrows} H_2O.$$

In this case, the experimental equation is:

$$\frac{d[B]}{dt} = k[S],$$

whence it follows that either Z_1 is a van't Hoff intermediate or both intermediates are of the Arrhenius kind. The observed equation would not be obtained here if the cation were Arrhenius, and Z_2 alone a van't Hoff intermediate. From the fact that, in both cases, the desired result is obtained when the cations are assumed to be van't Hoff intermediates, Skrabal concludes that, in all probability, the velocity is always determined by the primary act, in acid catalysis the absorption of the proton. It should be added, of course, that, generally, only Arrhenius intermediates are of use in the second stage.

We have already seen, in the case of hydrolysis, for example, that the view under discussion is by no means limited to pure prototropy, and it is also not confined to cases in which acid and base catalysis simultaneously lie within measurable bounds. Indeed, Skrabal (see p. 119) was able to show that these are only special cases of the general catenary. Thus, as Brönsted [130] pointed out, the efficiency of all acids and bases can be defined afresh even for " pure " acid and " pure " basic catalysis. The hydrolysis of ethyl orthoacetate, a reaction which is only catalyzed by acids and not by bases, was investigated by Wynne-Jones,[130] working in Brönsted's laboratory. He found a distinct effect produced by undissociated weak acids in the capacity of donors.

In the case of the decomposition of nitramide in aqueous solution, the reverse relations hold. The reaction is catalyzed by bases only,[174a] and follows the equation:

$$H_2N \cdot NO_2 \rightarrow H_2O + N_2O.$$

The kinetics can be conveniently followed by measurement of the N_2O gas produced. This was performed by Brönsted and Pedersen,[175] who found a whole series of bases effective, independently of whether the base was negatively charged, as, for example, the hydroxyl ion, acetate ion, and other acid anions, or neutral, like aniline and other amines, or positively charged, such as $[Co(NH_3)_5OH]^{\cdot\cdot}$, etc. We shall return to the discussion of the quantitative results later (p. 129).

The researches of Kuhn and Jakob [166] and Lowry and Smith [159] on the catalysis of the mutarotation of glucose have been considerably extended

[174a] Concerning a possible but still uncertain acid catalysis of this reaction, see C. H. Marlies and V. K. LaMer, *J. Am. Chem. Soc.*, **57**, 1812 (1935).

[175] J. Brönsted and K. Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

by Brönsted and Guggenheim,[176] from the same point of view. They measured the progress of the reaction by the change in volume of the solution in a sensitive dilatometer, instead of following the alteration in rotation, as their predecessors had done. Their results are particularly valuable and reliable, because the authors satisfied themselves of the absence of a primary salt effect (see p. 132), as indeed is to be expected in a reaction with one uncharged partner (see p. 140).

As regards acid catalysis, they not only found hydroxonium to be effective, but also the undissociated molecules of weak acids. The experiments were carried out in a p_H range where the hydrogen ion catalysis is negligible compared to the horizontal portion of the catenary due to water molecule catalysis, namely $p_H > 4$. A constant concentration of buffer salt was maintained, giving a constant concentration of anion, and the acid concentration was varied. It is clear that this method suffers from the dilemma that very weak acids are also weak catalysts (see below and p. 107), while stronger acids cannot be followed to very high concentrations without the H_3O^+ catalysis coming in.

The first examples to be investigated among bases were the anions of weak acids. As in Dawson's first method (p. 112), the salt concentration was varied with constant acid concentration, and the velocity was found to increase linearly with the anion concentration. Uncharged bases, such as pyridine (aniline forms a molecular compound, which complicates matters), and the NH_3 molecule also catalyzed the reaction, as well as various cobalti- and chromo-hydroxo-complexes, many of which have an even greater effect as bases than the hydroxonium ion as acid. Investigation of very weakly acid sulphate solutions showed that the sulphate ion is also a catalyzing base.

Brönsted's numerical data [130] have led to extremely interesting results as to the *connection between catalytic efficiency and acid or base strength.* It will be remembered that Snethlage [146] had already recognized that the undissociated molecules of the strongest acids are the best catalysts, and furthermore, that Taylor [150] expressed this rule in the formula:

$$k = aK^{0.5}$$

These results can be understood when it is considered that easily dissociated acid molecules must also be good proton donors.

According to the new definition of acid and base, we have now to define the acid constant,

$$K_s = \frac{\text{Base} \cdot OH_3^+}{\text{Acid}}.$$

[176] J. Brönsted and E. A. Guggenheim, *J. Am. Chem. Soc.*, **49**, 2554 (1927).

If the acid is an acid in the old sense, this expression becomes equal to the old acid constant. If the acid is a cation, for example, the ammonium ion, it then becomes:

$$K_s = \frac{NH_3 \cdot OH_3^{\cdot}}{NH_4^{\cdot}} = \frac{NH_3 \cdot K_w}{NH_4^{\cdot} \cdot OH'},$$

and therefore equal to the hydrolysis constant of the base. The reverse relationships hold for the basic constants. It is now only necessary to give special definition to the acid and basic constants of water. We have first:

$$K_s = \frac{OH' \cdot OH_3^{\cdot}}{H_2O} = \frac{K_w}{55.6} = 1.8 \times 10^{-16},$$

since the molarity of water in the homogeneous phase is 55.6. This constant is, at the same time, the basic constant K_b for the hydroxyl ion.

The basic constant of water, on the other hand, is:

$$K_b = \frac{OH_2 \cdot OH_3^{\cdot}}{OH_3^{\cdot}} = 55.6,$$

which is at the same time the acid constant of hydroxonium. The logarithms of the constants are 0.26 − 16 and 1.75 respectively.

The acid equilibrium constants defined in this way, are in their turn the quotients of the velocity constants of dissociation and association.

$$K_s = \frac{k_d}{k_{as}}.$$

If it is now assumed that within a series of acids, the variation in k_s depends on a similar variation of k_d and on an opposed alteration in k_{as} and, further, that the catalytic constant of the acid is related to k_d, that is, to the readiness with which protons are furnished, by a proportionality factor F, characteristic of the reaction, we should expect the following relation to hold:

$$k_s = F_1 \cdot K_s^x,$$

where x is a proper fraction. The agreement with Taylor's relationship (p. 109) is evident. Taking logarithms, we have:

$$\log k_s = \log F_1 + x \log K_s.$$

Similarly, for basic catalysis:

$$\log k_b = \log F_2 + y \cdot \log K_b,$$

or

$$\log k_b = \log F_2 - y \cdot \log K_s,$$

since $\log K_b$ of a base (anion) is equal to $-\log K_s$ of the corresponding

acid. These linear relationships hold very well for the hydrolysis of orthoacetate, the decomposition of nitramide (p. 126) and mutarotation. In Fig. 17, the velocity of orthoacetate hydrolysis is plotted logarithmically against the acid constants of the catalysts.

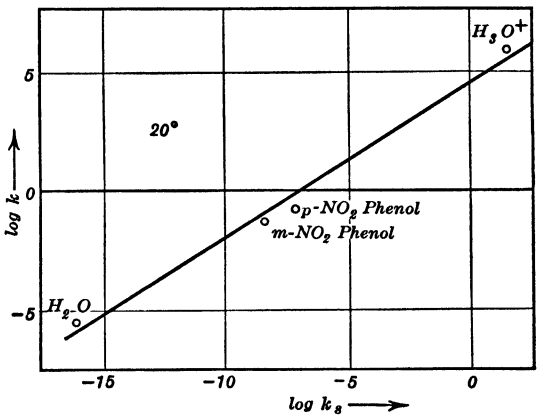


FIG. 17. Acid Catalysis in the Hydrolysis of Ethyl Orthoacetate as a Function of Acid Strength (Brönsted).

A similar curve for the basic catalysis of the decomposition of nitramide by acid anions is shown in Fig. 18. The abscissae represent the negative logarithms of the basic constants, that is, the logarithms of the dissociation constants of the acids primarily concerned. The equation is:

$$k_b = 6.2 \times 10^{-5} \cdot K_b^{0.85}$$

The velocities of the same reaction, catalyzed by neutral molecules (amine bases) are shown in Fig. 19. The abscissae again represent negative logarithms of the basic constants. The position of the straight line obtained in Fig. 18 is shown by the broken line, and from the close proximity of the two curves, it appears that there is practically no difference between simple negatively charged, and neutral bases. In this case, the velocity expression is:[176a]

$$k_b = 1.7 \times 10^{-4} \cdot K_b^{0.75}.$$

Brönsted[176b] has also shown that a series of positively charged bases (hydroxo complex cations) also give results which lie on a straight line, and that the velocity is given by:

$$k_b = 4.5 \times 10^{-3} \cdot K_b^{0.84}.$$

[176a] J. Brönsted and H. C. Duus, *Z. physik. Chem.*, **117**, 299 (1925).
[176b] J. Brönsted and K. Volqvartz, *Z. physik. Chem.*, A **155**, 211 (1931).

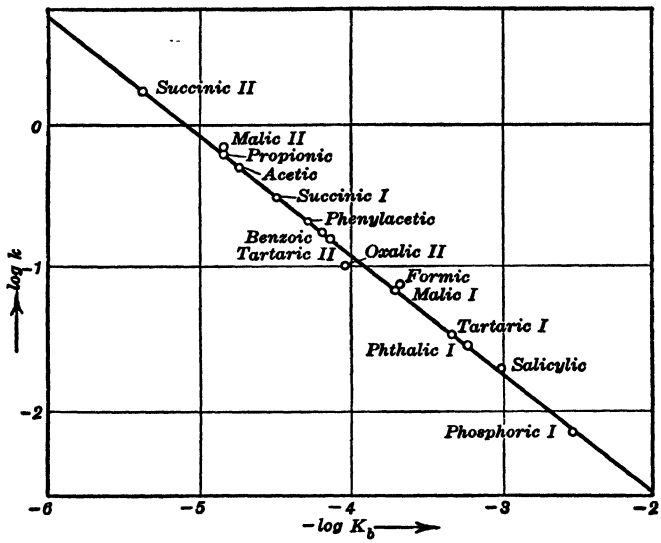


FIG. 18. Basic Catalysis of Nitramide Decomposition by Anions as a Function of Base Strength (Brönsted).

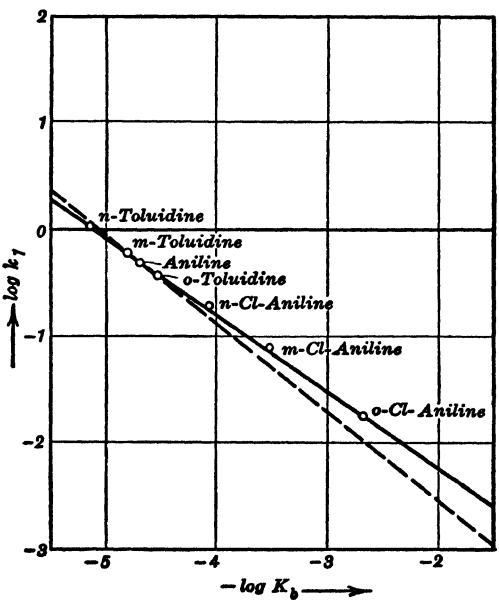


FIG. 19. Basic Catalysis of Nitramide Decomposition by Neutral Molecules as a Function of Base Strength (Brönsted).

It appears from these three equations, that the value of the coefficient depends largely on the catalyst charge, while the exponent, i.e., the slope of the curves, is approximately the same in every case.

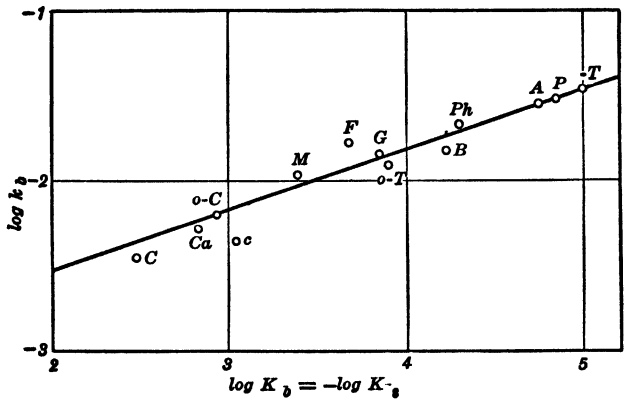


FIG. 20. Basic Catalysis of Mutarotation by Acid Anions as a Function of Base Strength (Brönsted).

Fig. 20 shows the mutarotation of glucose in relation to the basic constants of a series of acid-anions.

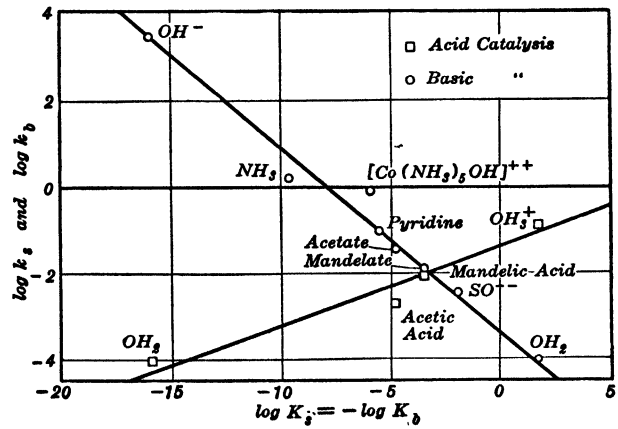


FIG. 21. Acid-base Catalysis of Mutarotation as a Function of Acid and Base Strength (Brönsted).

Finally, the mutarotation constants of a number of acids are represented in the positively inclined curve shown in Fig. 21, and the velocity constants of a series of bases are marked on the line with negative slope.

Apart from the positively charged, basic ion $[Co(NH_3)_5OH]^{\cdot\cdot}$, both series of results lie on straight lines, and a particularly noteworthy feature is that the amphoteric character of water is directly evidenced here by the fact that the value for water catalysis lies equally on the curves for acid and basic catalysis.

Moreover, if we take into consideration the curve drawn by Taylor, shown in Fig. 14, in which inversion, ester hydrolysis, enolization, esterification in alcohol, and decomposition of diazoacetic ester are included, it cannot be denied, even in the face of certain inexactitudes, that the relationship between catalysis and electrolyte strength or proton affinity has been established over a wide range. Finally, Brönsted and Bell [176c] have shown that the equation $k_s = F \cdot K_s^x$ holds for a series of carboxylic acids in the catalysis of the reaction between diazoacetic ester and phenol in benzene solution. In this case the catalyst is the undissociated acid molecule. Picric acid proved to be an exception to the above equation, however, and Brönsted suggests that, in solvents of low dielectric constant, the influence of the rest of the acid molecule will be much greater than in water and thus the equation may only hold for acids of the same chemical type.

It appears, therefore, that the many sided and frequently contradictory theories regarding homogeneous catalysis in solution, can be combined in one conception containing all the important features, which conception holds the key to the general understanding of this field of phenomena.

[176c] J. Brönsted and R. P. Bell, *J. Am. Chem. Soc.*, **53**, 2496 (1931).

CHAPTER VII

HOMOGENEOUS CATALYSIS IN SOLUTION. III

The Catalytic Salt Effect

Thus far, little mention has been made of the salt effect, a phenomenon which has frequently rendered the previous investigations more difficult, and which is itself of fundamental importance in regard to catalysis in aqueous solution. It is found that the catalytic efficiency of a molecular species or the velocity of reaction in general, is not independent of the components of the solution, and that the total ionic content, whether of the reactants or of added substances is especially important in this respect. Since the effect of neutral salts in acid-base catalysis is particularly striking, we also speak in this connection, of the " neutral salt effect."

Such an effect is of interest here for two reasons. Firstly, because it influences the efficiency of many catalysts, and secondly, because any alteration in the velocity of a reaction, whether catalytic or not, induced by the presence of salts, is itself in accordance with the definition of catalysis.

The Primary Salt Effect

In the first place, the effect which is due specifically to the addition of salts having an ion in common with the catalyst or substrate, and which can be explained on a mass action basis, will not be discussed here. Reference has already been made to this "secondary' salt effect (pp. 93, 112) and it will be dealt with in more detail later. Effects that depend on the ionic strength of the solution in general, are termed "primary salt effects," and can be brought about by electrolytes of foreign ions.

The effect has been known as long as ion catalysis itself. As early as 1889, in his first study in this field, Arrhenius [107] observed that added neutral salts increase the velocity in proportion to their concentration, and also that, with increasing acid concentration, the velocity increases more rapidly than the hydrogen ion concentration. The increase with the acid concentration may be expressed by:

$$k = a.m + b.m^2,$$

where k is the constant for cane sugar inversion and m is the concentration

of acid (see also p. 110). Arrhenius explained this in rather a modern way by assuming that the quadratic term represented the catalysis of the "active" cane sugar by hydrogen ions, both concentrations being proportional to the acid concentration. Later,[126] he attempted to replace the concentration of sugar in his calculations, by the osmotic pressure, a factor which is more nearly related to the thermodynamic activity (see below).

This conception was also incorporated by Euler [160, 161] in the theory of interacting ions, according to which the substrate ions are the active state of the substrate. He assumed that the foreign ions not only increase the osmotic pressure of the interacting ions, but also the dissociation of the substrate and the water.

The specific influence of strong electrolytes on the velocity was also observed by Fränkel,[138] Price [119b] and others, soon afterwards. Deviations from duality calculated according to the law of mass action, were observed at high acid and salt concentrations in esterification in alcohol by Goldschmidt and Sunde,[133] and in the decomposition of diazoacetic ester by Braune.[144]

The Activity Concept: These results obtained a more systematic treatment, on a theoretical basis, when the classical Arrhenius conception of the theory of strong electrolytes was abandoned in favor of complete dissociation and electrostatic interaction, as a result of the work of Milner, Bjerrum, Lewis, and others. According to the new theory, when the concentration of one mol ion is changed from c_1 to c_2, the amount of work involved is less than that expended in the case of neutral molecules (in ideal solutions):

$$A = RT \ln \frac{c_2}{c_1},$$

owing to the electrostatic interaction of the ions, and can be represented by:

$$A' = RT \ln \frac{c_2 f_2}{c_1 f_1}.$$

The work due to interionic repulsion is therefore:

$$A - A' = RT \ln \frac{f_1}{f_2}.$$

The factors are a measure of the "activity" of the ions, as compared with that of the neutral molecules at the same concentration and have been termed "activity coefficients." The product:

$$c \cdot f = a,$$

is called the " activity." At infinite dilution, where the interaction disappears, $f = 1$, and $c = a$.*

Owing to the appearance of " activities " in the work expressions, the van't Hoff reaction isochore derived under such circumstances does not lead to the classical mass action equation (concentration mass action law):

$$K_c = \frac{c' \cdot c'' \ldots}{c''' \cdot c'''' \ldots},$$

(where c is the equilibrium concentration of each reactant), but to:

$$K_a = \frac{c' \cdot c'' \ldots f' \cdot f'' \ldots}{c''' \cdot c'''' \ldots f''' \cdot f'''' \ldots}.$$

The activity coefficients f, of separate ionic species, are functions of the ionic strength of the solution, which will be defined more exactly later (see p. 142).

We have now to consider the application of these concepts to velocities. The problem is to separate the thermodynamic equation into two kinetic velocity expressions, with the help of special assumptions, analogous to Guldberg and Waage's classical resolution of the concentration-mass action equation into two concentration functions of velocities (see p. 17). As van't Hoff indicated, the simplest way to do this is to let each velocity depend only on the activities of its initial reactants, and therefore to put:

$$+\frac{dx}{dt} = k_1 c' \cdot c'' \ldots f' \cdot f'' \ldots,$$

and

$$-\frac{dx}{dt} = k_2 c''' \cdot c'''' \ldots f''' \cdot f''''.$$

When these velocities are equated, we obtain the thermodynamic equilibrium expression. It must be emphasized, however, that this does not prove the above assumptions to be correct, since the same result can be obtained with other assumptions. They must be considered rather as a possible solution, and it remains to prove whether the thermodynamic activity, fc, at the same time effectively represents the " kinetic activity."

Activity and Reaction Velocity: Various experiments have been undertaken in this direction, especially by Harned and Åkerlöf. These investigators compared the catalytic activities (velocity at unit concentration) of the ions with their activities derived from electromotive force.

* These considerations apply to ideal conditions, and the activities of the separate ions are used throughout, although only the activities of the whole electrolyte are thermodynamically determinable.

Thus, in the case of the reaction:

$$C_6H_5-\underset{\dot{Cl}}{N}-COCH_3 + H^{\cdot} + Cl' \rightarrow C_6H_5\cdot\underset{\dot{H}}{N}\cdot COCH_3 + Cl_2$$

$$\rightarrow C_6H_4Cl\cdot\underset{\dot{H}}{N}-COCH_3 + H^{\cdot} + Cl',$$

(see also p. 109), Harned and Seltz [178] found that, with varying acid concentration, the velocity per mol of hydrochloric acid is proportional to the square of the activity coefficients of the acid (i.e., $f_{H^{\cdot}} \cdot f_{Cl'}$), and like these, shows a minimum at about 0.5 normal acid. However, in a similar series of experiments with additions of neutral salt, the activities are not in agreement with the velocities under the same conditions.[178a]

Likewise, according to Harned and Pfanstiel,[179] the velocity of ester hydrolysis shows a minimum in the neighborhood of the minimum of the activity coefficient of the hydrogen ion (between 0.07 and $0.3n$). However, Dawson and Lowson [179a] have studied the reaction over a very wide range of HCl concentrations (0.0002 – 0.5 normal) and find that the rate is entirely proportional to the concentration of hydrogen ions. The specific catalytic activity of the latter, therefore, does not pass through a minimum as would be expected if it were proportional to its thermodynamic activity.

These results refer essentially to the variation in ionic strength produced by the catalyst acid itself, so Åkerlöf accordingly turned his attention [180, 181] to the addition of salts. In the case of ester hydrolysis, he found that a definite velocity is attached to each activity of the hydrogen ion, independently of the salt addition by which it is obtained. However, the connection does not appear to be linear, but is represented by the equation:

$$k = C\sqrt[3]{c_{H^{\cdot}} \cdot f_{H^{\cdot}}}.$$

Grube and Schmidt [182] have shown that this formula is a special case of a more general equation:

$$v = C'(c_{H^{\cdot}} \cdot f_{H^{\cdot}})^n,$$

which has been confirmed by their own measurements of the hydrolysis of cyanamide to urea, and by the experiments of Harned, Åkerlöf, Hantzsch,

[178] H. S. Harned and H. Seltz, *J. Am. Chem. Soc.*, **44**, 1475 (1922).
[178a] J. W. Belton, *J. Chem. Soc.*, 116 (1930).
[179] H. S. Harned and R. Pfanstiel, *J. Am. Chem. Soc.*, **44**, 2193 (1922).
[179a] H. M. Dawson and W. Lowson, *J. Chem. Soc.*, 2146 (1928).
[180] G. Åkerlöf, *Z. physik. Chem.*, **98**, 260 (1921).
[181] G. Åkerlöf, *J. Am. Chem. Soc.*, **48**, 3046 (1926).
[182] G. Grube and G. Schmidt, *Z. physik. Chem.*, **119**, 19 (1926).

and others. It is to be observed, however, that Åkerlöf's constant C is subject to very considerable variation from one salt to another, as well as with different acid concentrations. Nevertheless, he concluded from the results that the efficiency of the ions is determined only by their thermodynamic activity.

The decomposition of diacetone alcohol:

$$H_3C-CO-CH_2O-CH(CH_3)_2 = 2(CH_3)_2\,CO,$$

catalyzed by hydroxyl ions (Åkerlöf [181]), shows a salt effect which is the reverse of that obtaining in the above mentioned catalysis by hydrogen ion, both in regard to the order and direction of the velocity in the presence of different salts. This was attributed to the fact that salts which increase the hydrogen ion activity lower the hydroxyl ion activity, so that, here also, the rate is determined by the activity of the ions.

Direct proportionality between reaction velocity and activity of the hydrogen ion (and of the substrate) was also established in the case of the inversion of sucrose by Jones and W. McC. Lewis.[183] Again, Kuhn and Jakob [166] noted the appearance of salt effects in the mutarotation of glucose, and took up the standpoint, as opposed to that of Brönsted (see below), that the velocity is determined only by the activity of the initial reactants.

This brief summary could very well be extended, but it is already evident that the simple conception that the activity of the reactants determines the velocity, leads to incorrect or at least disproportionate results. This has recently been admitted by Harned and Åkerlöf themselves,[184] who now incline more to the views of Brönsted, discussed below. They show, at the same time, that, at higher concentrations, different reactions generally behave very differently.

The Brönsted Concept: With the help of the theory of strong electrolytes, it is possible to split up the equilibrium expression in another way, and a formula has been obtained, which is theoretically and experimentally satisfactory, in dilute solution at least. The development of this new theory of the primary salt effect is due to Brönsted.[185]

He supposes, to begin with, that two reactants, catalyst and substrate for instance, first of all collide together to form a complex of maximal instability, and that the velocity determining step in every reaction (even elementary reactions) is the formation of this so-called "critical complex."

[183] G. M. Jones and W. McC. Lewis, *J. Chem. Soc.*, **117**, 1120 (1920).
[184] H. S. Harned and G. Åkerlöf, *Trans. Faraday Soc.*, **24**, 666 (1928).
[185] J. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

The complex is not supposed to be in equilibrium, but is only a transitory state between the initial and final systems. Accordingly, a reaction $A + B \rightarrow D$, is written:

$$A + B \rightarrow AB \rightarrow D,$$

and in the reverse direction, $D \rightarrow AB \rightarrow A + B$. (AB may be represented by X, and such critical complexes are termed "X states.") Naturally, AB is an improbable state. It is assumed that the probability of transition into such a state depends on the potential difference, i.e., depends on:

$$RT\, ln \frac{f_A f_B}{f_{AB}}.$$

On the other hand, the transition from improbable into probable states (D), has a constant probability of 1. Hence, the first process determines the velocity (X is a van't Hoff intermediate), and the reaction velocity is given by the product of the collision number and the probability of transition:

$$\frac{d[D]}{dt} = k \cdot c_A \cdot c_B \cdot \frac{f_A \cdot f_B}{f_{AB}}.$$

The essential difference as compared with the van't Hoff treatment of the equilibrium expression is that here the activity of the critical complex appears in the denominator.

We have to satisfy ourselves, of course, that this formulation does not affect the conditions for thermodynamic equilibrium. This is seen to be the case when we introduce the same critical complex in the reverse reaction $D \rightarrow A + B$. We then obtain:

$$\frac{-d[D]}{dt} = k' \cdot c_D \cdot \frac{f_D}{f_{AB}},$$

and, equating both velocities:

$$\frac{c_A \cdot c_B}{c_D} \cdot \frac{f_A f_B}{f_D} = \frac{k'}{k} = K.$$

as required. It may be remarked that LaMer has recently raised a query [185a] as to the use of thermodynamic activity coefficients kinetically, because the 'entropy of activation,' that is to say, the temperature coefficient of the measured activation energy due to different transition probabilities at differing energy contents of reacting complexes, is not taken into account. This is, however, a refinement which generally will be within the large error of experiment.

[185a] V. K. LaMer, *J. Am. Chem. Soc.*, **55**, 1739 (1933).

The fraction $f_A f_B / f_{AB}$, comprising the correction to the classical formula, is termed the " kinetic activity factor " F.

In order to evaluate this, it is necessary to know the activity coefficients of the ions or molecules taking part in the reaction. In the first approximation these are dependent only on the charge (valence) of the ions concerned and on the foreign ions which supply essentially the ionic strength of the solution. Once determined, therefore, they are taken as the mean for all ions having the same charge, i.e., individual differences are neglected. The activity coefficients were first derived from measurements of the influence of additions of other salts to the solvent, on the solubility of difficultly soluble salts. The following figures were obtained in this way:

TABLE XX — ACTIVITY COEFFICIENTS

c	f_0	f_1	$f_{2(1)}$	$f_{2(2)}$	$f_{3(1)}$	$f_{3(2)}$
0.01	1.00	0.85	0.81	0.63	—	—
0.02	1.01	0.81	0.72	0.53	0.30	0.17
0.05	1.02	0.76	0.57	0.39	0.19	0.08
0.1	1.04	0.70	0.43	0.29	0.11	0.04

The first subscript indices refer to the valence of the ion in question, those in parenthesis refer to the oppositely charged ion of the medium, and c is the equivalent concentration of the latter.

In the first place, it is evident that only the smaller concentrations are considered here and that the minima of the activity coefficients in 0.3 to 0.5 molar solution considered by Harned, do not lie within the range of this theory, which is confined to dilute solutions. Furthermore, Harned's simple activity theory would clearly allow only *negative* salt effects in the region under consideration, since the activity coefficients decrease with the salt concentration. Actually, however, the velocity is just as frequently increased (see later).

The true salt effect is obtained when these activity coefficients are substituted in the kinetic activity factor F. The critical complex is considered simply as an ion whose charge is given by the algebraic sum of the charges of the ions from which it is formed. For example, in the reaction between ferric ions and iodide ions, the velocity determining step is assumed to be:

$$Fe^{\cdot\cdot\cdot} + I' \rightarrow (FeI)^{\cdot\cdot},$$

and therefore the kinetic activity factor is written:

$$F = \frac{f_3 \cdot f_1}{f_2}.$$

A similar critical complex is supposed to be formed in every homogeneous catalytic process, between the catalyst ions and the substrate ions or molecules. Different types of reactions can be distinguished according to the charge on the reacting ions as shown in the accompanying table. The resulting types are illustrated in Fig. 22, which shows the variation of F with concentration for different charge relations.

TABLE XXI — KINETIC ACTIVITY FACTORS

Charge of reactants		Charge of medium ions	F	Type	
		Ions of the same sign			
0	n		f_0	0	
1	1	1	$f_1^2/f_{2(1)}$	I	1
1	1	2	$f_1^2/f_{2(2)}$	I	2
1	2	1	$f_1 f_{2(1)}/f_{3(1)}$	II	1
1	2	2	$f_1 f_{2(2)}/f_{3(2)}$	II	2
		Ions of the opposite sign			
1	1		f_1^2/f_0	VI	
1	2	1	$f_{2(1)}$	VII	1
1	2	2	$f_{2(2)}$	VII	2
1	3	1	$f_1 f_{3(1)}/f_{2(1)}$	VIII	1
1	3	2	$f_1 f_{3(2)}/f_{2(2)}$	VIII	2
2	2	1	$f_{2(1)}^2/f_0$	IX	1
2	2	2	$f_{2(2)}^2/f_0$	IX	2
2	2	1 : 2	$f_{2(1)} f_{2(2)}/f_0$	IX	12
2	3	1	$f_{2(1)} f_{3(1)}/f_1$	X	1
2	3	2 : 1	$f_{2(2)} f_{3(1)}/f_1$	X	21
2	3	1 : 2	$f_{2(1)} f_{3(2)}/f_1$	X	12
2	3	2 : 2	$f_{2(2)} f_{3(2)}/f_1$	X	2

It is obvious that Types I and II, i.e., reactions between ions of the same sign, show a positive salt effect, while Types V to X, reactions between oppositely charged ions, show a negative salt effect. On the other hand, reactions occurring between ions and neutral molecules have practically no salt effect, because the activity coefficients of the ions and the equally charged critical complex cancel out, while that of the neutral molecules is practically unity (see p. 142 for details).

Brönsted shows that these deductions agree with the results of investiga-

tions of a whole series of reactions. First of all, he considers Arrhenius' measurements of the inversion of cane sugar.[107] It is immaterial whether the reaction is represented by:

$$Z + H^{\cdot} \rightarrow ZH^{\cdot};$$
$$ZH^{\cdot} + H_2O \rightarrow D + L + H^{\cdot},$$

or

$$Z + H^{\cdot} \rightleftarrows ZH^{\cdot};$$
$$ZH^{\cdot} + H_2O \rightarrow D + L + H^{\cdot},$$

where D = dextrose and L = laevulose, as, in both cases, the velocity determining reaction, in the former, the first, in the latter, the second, is of the ion-neutral molecule type. The salt effect, therefore, should not be greater than the increase in the activity of such neutral molecules, and according to the table given on p. 139, this only amounts to about 4% in 0.1 normal electrolyte solutions. Actually, an increase of 3–4% is found experimentally. Similar results can be obtained for the hydrolysis of diazoacetic ester investigated by Bredig. The decomposition of nitramide under the influence of the base, H_2O, behaves similarly, the salt effect in 1-molar alkali chloride solution reaching only 20 per cent.[185b] The same is true also for the enolization of aceto-acetic ester.[185c] The effect depends simply upon a fixing of the water as an ion-hydrate envelope. Ester hydrolysis should behave in

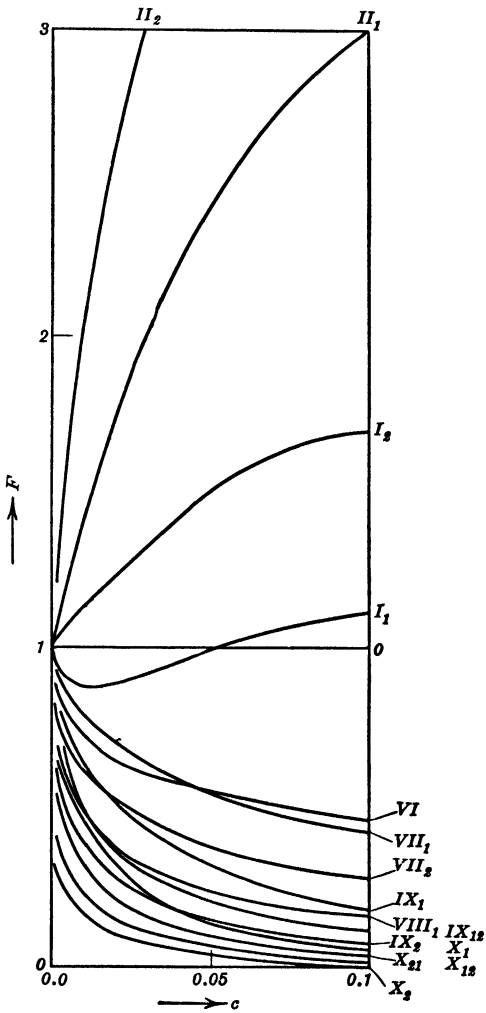


FIG. 22. Kinetic Factor as a Function of Concentration for Various Types of Reaction (Brönsted).

[185b] C. A. Marlies and V. K. LaMer, *J. Am. Chem. Soc.*, **57**, 1812 (1935).
[185c] K. Pedersen, *J. Phys. Chem.*, **37**, 751 (1933).

the same way, but instead, shows a slight (2%) inhibition by salts, owing to the fact that the activity coefficients of OH′ and the ester anion EOH′ are not exactly the same. We may call this difference a specific influence.

Of the reactions discussed by Brönsted showing a larger salt effect, only the reaction between persulphate and iodide, investigated by Price[119b] will be mentioned here. Since the critical complex is formed from $S_2O_8'' + I'$, it belongs to Type II. According to Fig. 22, in a solution of univalent cations (II, I), the velocity constant (calculated from concentrations) should increase 1.8 times, between salt concentrations of 0.02 and 0.10. A ratio of 2.0 was found experimentally. A more exact study of this reaction has more recently been made by von Kiss and Bruckner.[186] They likewise find that it agrees with the predictions of the theory. However, they also find a specific variability of the activity coefficients, particularly in the presence of an oppositely charged medium ion. This is not surprising, in the light of the stricter theory, and Brönsted himself, who discussed a large number of other reactions in confirmation of his theory, obtained similar results.

In a later paper, Brönsted [187] discussed his theory in relation to the Debye-Hückel theory of strong electrolytes, which had been put forward in the meantime. This, of course, allows the activity coefficients to be predicted theoretically, for very dilute solutions. Neglecting the ionic radii, the theory (see, for example, Hückel [188]) gives the following expression which is generally satisfactory for the region of low concentrations:

$$\log f = -\frac{\epsilon^2 z^2}{2DkT}\kappa,$$

where κ has the dimensions of a reciprocal length and is a measure of the electrostatic field of the individual ions. It is equal to:

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT}}\ \sqrt{\sum nz^2}$$

In this equation, ϵ is the elementary charge, z is the valence of the ions, D the dielectric constant, k the Boltzmann constant, T the absolute temperature, and n the number of ions of each species per cubic cm. The quantity $\sum nz^2$ represents the ionic strength (see Lewis and Randall,[188a] and p. 135). For a single univalent salt, it is equal to double the normality, or in a solution with a large excess of added salt, equal to twice its concentration. Col-

[186] A. v. Kiss and V. Bruckner, *Z. physik. Chem.*, **128**, 71 (1927).
[187] J. Brönsted, *Z. physik. Chem.*, **115**, 337 (1925).
[188] E. Hückel, *Erg. exakt. Naturwiss.*, **3**, 243 (1924).
[188a] G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1141 (1921).

lecting the constants in both equations, we obtain the expression:

$$\log f = -0.5z^2 \sqrt{c},$$

which Brönsted and LaMer [189] were able to verify experimentally for very dilute solutions. The empirical activity coefficients used above (p. 139) can now be justified theoretically, for high dilutions at least. We obtain for the total kinetic activity factor F:

$$\log F = \log f_A + \log f_B - \log f_{AB} = -0.5\,(z_A^2 + z_B^2 - z_{AB}^2)\sqrt{c},$$

and, since

$$z_{AB} = z_A + z_B,$$

$$\log F = z_A \cdot z_B \sqrt{c},$$

or

$$F = 10^{z_A \cdot z_B \sqrt{c}}.$$

It was inferred on p. 140, from the separate empirical activity coefficients, that reactions between ions of the same sign have a positive salt effect, reactions between ions of opposite sign have a negative salt effect, and reactions of neutral molecules have none. This was found to be verified by experiment and now follows theoretically from the above equation, since it introduces the algebraic product of the ionic valencies, with their appropriate sign.

It appears, furthermore, that the salt effect increases exponentially with the square root of the concentration, as long as the solutions are very dilute, when the underlying equations are operative. Consideration of Fig. 22 would show that this is actually the case. Brönsted termed this the "exponential salt effect."

For the case in which the medium ions, of opposite sign to the substrate ions, are multivalent, the Debye-Hückel theory is to be employed in the extended form developed by LaMer, Gronwall and Greiff.[189a] The dependence of the activity coefficients on the square root of the ionic strength is, in presence of such ions, two to three times as great as that given in the approximation employed above. LaMer and Fessenden [189b] experimentally find such characteristic differences in the salt effect of uni- or multivalent electrolytes, of the order of magnitude expected.

The form of the Debye-Hückel theory which we have employed so far only holds as a limiting rule for extremely dilute solutions, where the characteristic length $1/\kappa$ is large compared with the ionic diameters. At

[189] J. Brönsted and V. K. LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

[189a] V. K. LaMer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931); see also V. K. LaMer, Gronwall and Sandved, *Physik. Z.*, **29**, 358 (1928).

[189b] V. K. LaMer and Fessenden, *J. Am. Chem. Soc.*, **54**, 2351 (1932).

greater concentrations, with larger screening effects by neighboring ions, this is no longer the case and the more general formula is used as the next approximation:

$$\log f = -\frac{\epsilon^2 z^2}{2DkT} \cdot \frac{\kappa}{1 + \kappa a'},$$

in which a represents the mean diameter of the ions. The first two terms of the expansion of the fraction which appears instead of κ are $\kappa - \kappa^2 a$. Hence, when κa is large, the next term in the expression for log f becomes linear in c (see Hückel,[188] pp. 224 and 245). From these considerations, Brönsted and LaMer [189] derived a corresponding formula containing two terms, which Brönsted [190] considers to be plausible because neutral molecules show a predominantly linear dependence of log f on c, an effect which can be assumed *a priori* in the case of ions to be superposed on the square root relationship. On the basis of these plausible considerations, and with the support of activity measurements, Brönsted formulated a more explicit equation, applicable to higher concentrations or large κa, as follows:

$$\log f = -0.5 z^2 \sqrt{c} - \beta c.^{130} *$$

According to this equation, the statement that reactions between neutral molecules and ions show no salt effect must be qualified. The first term, indeed, is zero, as has already been shown on p. 143, since $z = 0$ for neutral molecules. The second term, however, corresponds to a salt effect measured by:

$$F = 10^{c(\beta_A + \beta_B - \beta_{AB})}.$$

(Compare footnote, however.) In the case where A is a hydrogen ion, and B a neutral molecule, β_A practically outweighs the other terms (including β_{AB}), and a salt effect in accordance with:

$$F = 10^{bc}$$

results. At large dilutions, when $bc \ll 1$, we can put:

$$F = 1 + 2{\cdot}30bc.$$

This indicates a linear salt effect [130] for hydrogen ion catalysis such as the above. This is actually the case in the inversion of sucrose, the decomposition of diazoacetic ester, and in ester saponification, as we established on p. 141, although in much smaller amount than the exponential salt

[190] J. Brönsted, *J. Am. Chem. Soc.*, **44**, 938 (1922).

* It is not very clear why the factor z^2, important in the subsequent discussion, has disappeared from the second term.

effect in pure ionic reactions. In special cases, however, such as the hydrolysis of ethylene oxide,[144] the linear salt effect becomes considerable.

Recent investigation of heats of dilution of salts [190a] has shown that a marked individuality can be attributed to the ionic effects, even at large dilutions, where it has previously been assumed that the Debye-Hückel conditions of a uniform charge effect hold exactly. Hence, any extension of the theory of the kinetic salt effect to concentrations greater than 0.1 normal, can only be regarded as preliminary, since it would have to be based on an approximate theory of strong electrolytes. A complete consideration of the correcting factors — ionic diameter, deformation properties, variation of dielectric constants — is a development rather to be looked for in the future. The progress of the theory of catalysis in this direction will, therefore, depend, as it has done in the past, on the development of the theory of electrolytes.

However, according to our present view, we can hardly expect anything very fundamental in regard to catalysis itself to be revealed in this way. There are certain things, of course, which still require an explanation, in particular, the different behavior of individual reactions at high concentrations, established by Harned and Åkerlöf (p. 135). After all, a great advance has already been made, in that the primary salt effect can be attributed to the influence of activity, and can be represented quantitatively for dilute solution.

Bjerrum's Approach to the Problem: We shall now take up the discussion of some other methods by which the theoretical basis of the generally accepted formula of Brönsted:

$$F = \frac{f_A \cdot f_B}{f_{AB}},$$

has been approached.

In the first place, Bjerrum [109] has given an interpretation to this equation which is contrary to Brönsted's conception of the critical X complex. He assumes an Arrhenius intermediate, or "S complex," which reacts in proportion to its concentration and not its activity. When this is in thermodynamic equilibrium with A and B, its concentration, and consequently its velocity of reaction must clearly be proportional to:

$$C_A C_B \cdot \frac{f_A f_B}{f_S}.$$

The Brönsted formula can therefore be strictly derived in this way, and we thus see that the ambiguity of the kinetic results extends to the salt

[190a] E. Lange and H. Streeck, *Z. Elektrochem.*, 37, 689 (1931).

effect. Bjerrum has also derived the same result kinetically. He calculates, in a cyclical process, the probability of existence in solution of a " constellation " AB of definite potential, and assumes that it will react further in proportion to its concentration. The expression obtained in this way becomes identical with the Brönsted combination of activity coefficient expressions derived from Bjerrum's theory of electrolytes.

Therefore, while Brönsted allows the velocity of formation of the complex to depend on activities, Bjerrum favors the " concentration hypothesis " according to which velocities are always proportional to concentrations, as in radioactivity, and he supposes, furthermore, that the ionic strength only determines the primary equilibrium. According to Brönsted the whole of the complex formed reacts to give D, and the temperature coefficient depends entirely on its rate of formation. On the other hand, according to Bjerrum, the subsequent reaction of the S complex is still strongly dependent on temperature. Both views are considered by LaMer [190b] who shows that comparison with radioactivity is scarcely permissible, as this concerns nuclear changes, and claims the S complex is not consistent with the existence of a salt effect in a reversible unimolecular reaction.

Christiansen's Derivation: The two conceptions were united in another derivation by Christiansen,[191] who deduced the equation in a more fundamental manner from the Debye theory. Analogous to Skrabal's general equation (see p. 72):

$$k = \frac{k_3 k_1}{k_2 + k_3},$$

he puts the reaction velocity equal to:

$$v = c'_A c'_B \cdot Z_{AB} \cdot \sqrt{T} \cdot e^{-q/RT} \cdot \Omega \frac{\rho}{\rho + \sum nc}$$

Here, $Z_{AB} \cdot \sqrt{T}$ is the gas kinetic collision number at unit concentration, q the energy of activation, Ω the " steric factor " of the order of magnitude 1, ρ the probability that the complex subsequently reacts, and $\sum nc$ the probability that it is deactivated to A + B by molecules of concentration c, each with a separate probability n. An important point here is that it is not the gross concentrations c_A and c_B that have to be taken into consideration in computing collisions, but the concentrations prevailing in the immediate neighborhood of the colliding ions, given by the Debye theory:

$$c'_A = c_A \cdot e^{-\epsilon z_A \phi_B / RT}$$

[190b] V. K. LaMer, *Chem. Reviews*, **10**, 179 (1932).

[191] J. Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

ϕ_B represents the potential round the ion B at the collision distance, for which we have:

$$\phi_B = \frac{\epsilon z_B}{D} \cdot \frac{e^{-\kappa a}}{a}$$

the same meaning being attached to the symbols κ and a, as on p. 144. The subsequent treatment of these expressions will only be indicated in brief. The constants, referred to concentrations, are introduced instead of the velocity, thereby removing the concentrations c in the original formula. The dependence of these " constants " upon concentration is then, except for a small factor (the summation terms in the log), the required dependence of F. Furthermore, $1-\kappa$ is put instead of $e^{-\kappa a}$, which is permissible when κ is small, i.e., in dilute solution again. After inserting the numerical value, the equation:

$$\log k = \log Z_{AB} + \log \alpha + \tfrac{1}{2} \log T - \frac{q}{4.6T} - \frac{3.07 z_A z_B}{a} + 1.003 z_A z_B \sqrt{\Sigma c z^2}$$

is finally obtained, where α represents $\frac{\rho}{\rho + \Sigma nc}$ and is treated as a constant.

We see at once that the last term, which is alone dependent on concentration, corresponds directly to the Brönsted expression for $-\log F$, previously derived on p. 138 from the separate activity coefficients. The Brönsted formula has therefore been shown to hold for the number of collisions generally. Finally, it is valid for a complex of A and B separated by a distance of a, and whether this is to be regarded as Brönsted's X complex, or as Bjerrum's equilibrium concentration of S, is more a matter of definition. The difference between the two conceptions is evidently connected with the expression α, which has not been very closely considered up to the present. If:

$$\Sigma nc \gg R$$

then the complex ion is in equilibrium with the initial reactants (Bjerrum), but, in the opposite circumstances, it reacts almost in every case before becoming deactivated (Brönsted). Christiansen himself endeavored to differentiate between the two possibilities by calculating a from experimental data, in accordance with his final equation. The values he obtained were about 100% too high, whence he concluded that α is less than unity, i.e., Σnc does not vanish, therefore rather favoring Bjerrum's S complex. It is questionable, however, whether the equation is sufficiently exact to enable this kind of differentiation to be made.

In any case, when specific inhibition by deactivation does appear, it preponderates with ions of the opposite sign (opposite to the complex and the

catalyst). It is only the latter, therefore, that develop any specific individuality apart from the ordinary relationships (see Brönsted,[185] v. Kiss and Bruckner,[186] and Holmberg, cited in [186]).

The Secondary Salt Effect

The results described in the preceding section show that the reaction velocity and especially the efficiency of the catalyst are generally altered by the presence of ions in the reaction medium. In addition to this primary salt effect, we have also noticed a specific influence of salts with common ions (p. 103), depending on the suppression of dissociation of the catalyst acid, and in this way affecting its efficiency. In the first approximation, this effect can be deduced from the classical law of mass action, as, indeed, it has been from the time of Arrhenius.

The hydrolysis of bromacetic acid ions, studied by Senter and Bulle [192] and Senter and Ward [193] is a good example, in which, moreover, the influence of some salts of foreign ions could be explained in this way. In alkaline solution, the reaction is accelerated about 100% by sodium formate, acetate, and tartrate, while ferrocyanide and chlorate are without influence. Investigation of the reaction in neutral solution with the addition of accelerating salts, shows that it does not take place in one step:

$$Br \cdot CH_2COO' + H_2O \rightarrow HO \cdot CH_2COO' + H^{\cdot} + Br',$$

but that the formation of acid occurs at a slower rate than the production of bromine ions. It appears, therefore, that the salt is involved in a primary equilibrium:

$$Br \cdot CH_2 \cdot COO' + H_3C \cdot COO' \rightleftarrows H_3C \cdot \underset{\underset{O}{\|}}{CO} - CH_2 \cdot COO' + Br'.$$

The intermediate is then saponified by water at a measurably slow rate:

$$H_3C \cdot \underset{\underset{O}{\|}}{CO} - CH_2COO' + H_2O \rightarrow H_3C \cdot COO' + HO \cdot CH_2 \cdot COO' + H^{\cdot},$$

but is rapidly saponified by hydroxyl ions:

$$H_3C \cdot \underset{\underset{O}{\|}}{CO} - CH_2COO' + OH' \rightarrow H_3C \cdot COO' + HO \cdot CH_2COO',$$

and the greater velocity in the salt solutions as compared with that in the

[192] G. Senter and F. Bulle, *J. Chem. Soc.*, **101**, 2528 (1912).
[193] G. Senter and T. J. Ward, *J. Chem. Soc.*, **101**, 2534 (1912).

salt free solutions is due to this reaction. In neutral solution, the concentration of the intermediate can be derived from the mass action equilibrium equation, and in alkaline solution the total increased velocity can be deduced according to the formula for successive first order reactions.

The success of the classical theory in this case led Senter [194] to attribute the salt effect in general to a mass action influence on an intermediate concentration. It was generally hoped at the time (see, for example, Abel [123]) that it would be possible to account for the salt effect in this way, on classical grounds, by the hypothesis of an intermediate compound. The primary and secondary salt effects had not, at that time, been clearly differentiated.

Those examples of the addition of salts with common ions, in which the mass action calculation gave results not in agreement with experiment, have claimed particular interest. Thus, the velocity of an acid catalysis could not be suppressed to zero by a salt of the acid, and it was from such observations that the existence of new effects was deduced, particularly with regard to anions and neutral molecules. The work of Goldschmidt, Braune, Snethlage, Dawson and others (see p. 101), which we have interpreted in this sense, will be recalled here.

However, the existence of a purely physical, general salt effect, leads us to expect deviations from the concentration mass action law, under all conditions. In consequence, we have now to discuss the question as to how far the conclusions, which had previously been drawn from such deviations, were not altogether mistaken, through the neglect of the primary salt effect. Unfortunately, this question has not yet been worked out in a uniform manner, on the basis of the fundamental experimental material, since the various authors have invariably treated the primary salt effect in the language of the activity theory and the secondary in more classical form, without considering both from the same point of view.

It must be noted that an existing secondary salt effect will always be accompanied by a primary effect. In the first place, the addition of a neutral salt of the same anion alters the ionic strength of the medium, and, according to Brönsted, this is accompanied by an alteration in the reaction velocity at a given concentration. The effect is to be observed in reactions involving neutral molecules in dilute solution, and, fortunately, the examples of acid-base catalysis which have been studied in most detail, such as mutarotation, inversion, saponification, enolization, decomposition of diazo compounds, belong to this class. The linear salt effect is considerable in such cases in more concentrated solution (90% in 3*n* NaCl). This change in

[194] G. Senter, *Z. physik. Chem.*, **70**, 518 (1910).

the catalytic efficiency can only be studied independently when the salt does not bring about any alteration in the dissociation of the catalyzing acid. Consequently, the investigation is limited to strong acids such as hydrochloric which are known to be completely dissociated in dilute solution.

However, in the case of acids so weak that an undissociated fraction has to be assumed, the alteration of dissociation through changes in the ionic strength has to be taken into consideration. This is likewise classed as a secondary effect, although exercised by salts of foreign ions.

Dawson and Key [195, 158] studied the effect in the following way. The influence of the salt on the catalytic activity was measured in solutions of hydrochloric acid known to be completely dissociated, where the hydrogen ion concentration [H$^+$] is equal to the analytical concentration of the acid. The k_H so obtained must also apply to a weak, partially dissociated acid at the same salt concentration, and therefore enters the equation (see p. 113):

$$v = (k_H + k_a - k_m)\,[H^+] + k_m c.$$

k_a and k_m in this equation were determined according to the methods given on p. 114, in the presence of the salt, and, in this way, [H$^+$] obtained. From this, the value of the dissociation equilibrium constant K of the concentration mass action equation can be calculated for a given concentration of salt. The variation in K reflects the influence of the salt on the dissociation equilibrium, while changes in the k values also make themselves evident.

Thus, for the enolization of acetone by acetic acid in the presence of sodium chloride or nitrate, k_H increases approximately linearly from 4.65 to 11 with salt concentration rising from 0 to 4 normal. Nevertheless, k_a and k_m remain practically unchanged, for, as Brönsted would express it, there is a strong specific linear salt effect for hydrogen ions in a reaction with neutral molecules (see p. 144) and none in the case of the other ions (anions) and acid molecules. The figures given in the following table are abstracted from Dawson's paper:

TABLE XXII — SALT EFFECTS ON k_H

c_{NaCl}	$k_H \times 10^4$	$k_a \times 10^6$	$k_m \times 10^6$	$K \times 10^5$
—	4.65	4.0	1.4	1.82
0.5	5.30	3.7	1.4	2.91
2.0	7.26	3.4	1.4	2.02
4.0	11.10	3.4	1.3	0.84

[195] H. M. Dawson and A. Key, *J. Chem. Soc.*, 1239 (1928).

Dawson [158, 196] shows that his methods for the determination of k_a and k_m by small additions of salts with common ions are independent of foreign salt additions. The values obtained by this method are trustworthy, therefore, whether foreign salts are present or not.

The hydrolysis of ethyl acetate in x molar sodium chloride solutions, catalyzed by a series of weak acids was studied by Dawson and Lowson.[196a] Analysis of the experimental results revealed the relation:

$$\log R_x = a\sqrt{x} - bx,$$

where $R_x = K_x/K_0$, the ratio of the ionization constants in molar solution and salt free solution. (K_0 is termed the limiting ionization coefficient in the absence of ionic effects.) Assuming that $K_a = K_x \frac{f_{\pm}^2}{f}$ (K_a is the activity dissociation constant), and making use of the Debye-Hückel equation for $f_{\pm}^2$, Dawson and Lowson derived the following equation for $\log R_x$:

$$\log R_x = 2\alpha\sqrt{x} - \beta x.$$

Clearly, both equations are of the same form. While, however, $2\alpha = 1.0$, the value of the empirical coefficient a is only 0.54. The reason for the divergence is at present not clear.

A very interesting application of this equation has been made by Dawson and Millet [196b] in a study of the intra molecular rearrangement of N-chloroacetanilide (see p. 109 and p. 136) catalyzed by hydrochloric acid. It had previously been shown by Belton [178a] that explanations put forward by Harned and Seltz [178] and Soper and Pryde,[196c] based on the activity rate hypothesis (see p. 136) break down when the neutral salt concentration is varied. However, if it is assumed that the active catalyst is the undissociated hydrochloric acid molecule, and that the ionic efficiencies are negligible in comparison, it is possible to account for the observed rate under widely different conditions of salt addition or acid concentration.

It was found first of all, that, while the value of coefficient a is the same whatever the (univalent) salt added, the value of b is different for each salt. The equation was therefore written:

$$\log R_x = a\sqrt{x + c} - bx - b'c.$$

[196] H. M. Dawson, in General Discussion, *Trans. Faraday Soc.*, 24, 724 (1928).
[196a] H. M. Dawson and W. Lowson, *J. Chem. Soc.*, 1217 (1929).
[196b] H. M. Dawson and H. Millet, *J. Chem. Soc.* (1932).
[196c] F. G. Soper and D. R. Pryde, *J. Chem. Soc.*, 2761 (1927).

The values finally adopted for the constants are $a = 0.56$, $b' = 0.42$ for $(H^{\cdot} + Cl')$, $b = 0.265$ for $(Na^{\cdot} + Cl')$ and 0.22 for $(Na^{\cdot} + NO_3')$. Representative results for $0.2n$ HCl are given in the following table:

TABLE XXIII

SALT EFFECTS IN ACID CATALYZED REARRANGEMENT OF N-CHLOROACETANILIDE

x $NaNO_3$	$k \times 10^3$	K_x/K_o	$k\,K_x/K_o[H^{\cdot}]\,[Cl']$
0	1.72	1.46	0.0626
0.5	1.37	1.88	0.0643
1.0	1.21	2.04	0.0618
3.0	1.39	1.805	0 0627
3.5	1.46	1.67	0.0610
x NaCl			
0.5	4.91	1.785	0.0626
1.0	8.48	1.84	0.0649
3.0	31.00	1.325	0.0641
3.5	39.5	1.16	0.0620

The constancy of $k\,K_x/K_o\,[H^{\cdot}]\,[Cl']$ is strong evidence in favor of catalysis by the undissociated acid and direct proportionality of the rate to its concentration rather than to the thermodynamic activity.

The results which led to the conception of anion and molecular catalysis, at least in their most recent form, are apparently immune from criticism on the basis of the new electrochemistry. All those investigations in which duality was established for catalysis of neutral molecules (mutarotation, enolization, etc.) retain their full significance, since, in the first approximation, such reactions have no salt effect in dilute solution. The validity of these results was demonstrated by the excellent work of Brönsted and Guggenheim [176] in which the results of Lowry and Dawson were confirmed and extended in the case of mutarotation, the absence of salt effect being expressly established. Similarly, the residual velocity after complete suppression of the dissociation of a weak electrolyte by salt with a common ion, is only to be accounted for by catalysis due to the undissociated molecule.

On the other hand, investigations in which such conclusions were based exclusively on the non-linear dependence of the catalysis on the catalyst concentration (e.g., Acree,[154] Hantzsch [145]) should be regarded with caution. The salt effect exercised by the ions of the catalyst itself can always be assumed here *a priori*, so that the validity of the explanation has to be ascertained in each case.

On the whole, therefore, the principal results obtained on classical grounds in regard to anion and molecular catalysis, and particularly the conception of acid-base catalysis which has developed from them, remain essentially unchanged by the discovery of the salt effect. However, as we have already indicated on p. 115, it is now necessary to bring about a more quantitative improvement.

CHAPTER VIII

HOMOGENEOUS CATALYSIS IN SOLUTION. IV

The Influence of the Solvent

Our previous considerations have been essentially confined to a study of the common characteristics of catalysis in different reactions, and the reaction medium, usually water, has been kept constant. If, on the other hand, we consider the same reaction in different media and establish differences in the velocity from one medium to another, then, according to definition, these must also be regarded as catalytic processes, even if the reaction can occur without the presence of dissolved " catalysts."

The influence of the solvent is closely allied to the special case, discussed in the previous chapter, in which the medium is varied by salt addition. However, we have now to deal with much wider variations, in which the effect is not so readily subject to theoretical treatment, because no longer restricted to charged molecules.

If we consider a genuine unimolecular reaction, such as the decomposition of nitrogen pentoxide, we arrive at the conclusion that the relative velocity of reaction in a solvent should be the same as in the gas phase. In these circumstances, the sole influence of the solvent is to permit the attainment of higher concentrations at the same temperature and thereby higher absolute velocities. In such processes (see p. 25), then, the velocity of activation by collision and its possible modification by collisions with the solvent are of negligible importance, and the reaction velocity is determined only by the energy conditions within the active molecules themselves. Actually, the racemization of pinene studied by Smith [197] and the decomposition of nitrogen pentoxide, studied by Lueck [198] appear to have approximately the same velocities in different solvents and in the gas phase. Rice and Sullivan [110] conclude, therefore, that this independence of medium is a general property of unimolecular reactions in solution, including the decomposition of a complex of catalyst and substrate. This view would be in accord with Bjerrum's " concentration hypothesis " [109] mentioned previously (p. 145), in which the S complex decomposes in proportion to its concentration, uninfluenced by the environment.

[197] D. Smith, *J. Am. Chem. Soc.*, **49**, 43 (1927).

[198] R. H. Lueck, *J. Am. Chem. Soc.*, **44**, 757 (1922).

When the problem is considered from a standpoint which is more closely related to that taken up in the preceding chapter, we find that an essentially different result is to be expected. It may be supposed, particularly in bimolecular reactions, that only the non-solvated molecules are of importance in the reactions. The effect of the solvent is thus comparable with the screening effect of the ions assumed in the theory of reaction velocity in electrolytes. Consequently, we are able to define an " activity coefficient " for such solutions.

For this purpose, we assign an activity of one to the saturated vapor of the dissolved substance. All saturated solutions of the same substance have then the same activity, since they must contain the same concentration of free molecules, that is to say, molecules upon which no force is exerted by the solvent. We have previously ascribed an activity of one to electrolytes in infinitely dilute solution, since then f only contains the influence of the ions and not that of the solvent. Now, however, it is the medium that is to be varied and ions will not be considered. The only difference between the two cases is in the zero point of $\log f$, or a constant factor in f, and hence there is no alteration in the form of the equation.

In the saturated solution, the solubility or saturation concentration L corresponds to an activity of 1, and accordingly, the ratio of free to solvated molecules is $1 : L$. The same ratio must also hold in more dilute solutions of concentration c (mass action law) as long as the solvent is in considerable excess. The concentration of free molecules now appears to be identical with the activity a. It follows therefore, that:

$$\frac{a}{c} = \frac{1}{L}.$$

According to this nomenclature, the activity coefficient must have the value:

$$f = \frac{a}{c} = \frac{1}{L},$$

that is, it is equal to the reciprocal solubility.

A similar definition can also be obtained, according to van't Hoff, from the following equilibrium consideration of Dimroth.[199] In the reaction:

$$A + B = C,$$

we have for the vapor phase:

$$K_1 = \frac{p_A p_B}{p_C},$$

[199] O. Dimroth, *Liebig's Ann.*, **377**, 127 (1910).

which also holds for the saturated vapors over the substances themselves or over saturated solutions. Furthermore, the total concentration in the saturated solutions (solvated + free), or, in other words, the solubility, is given by the Nernst-Henry distribution theorem:

$$L = S.p.$$

From this it follows that:

$$\frac{L_A L_B}{L_C} = K_1 \cdot \frac{S_A S_B}{S_C} = K_2.$$

The concentration mass action equation for any dilution in any solvent is:

$$K_m = \frac{C_A C_B}{C_C}$$

and, on division by the previous expression, we obtain:

$$\frac{C_A C_B}{C_C} \cdot \frac{L_C}{L_A L_B} \frac{K_m}{K_2} = \frac{a_A a_B}{a_C} = K_3,$$

which is the activity mass action equation. Since it is the equilibrium between the " free " molecules that is considered, the constant K_3 must be independent of the solvent. Dimroth [199] therefore termed it the " absolute " equilibrium constant.

As in the case of electrolytes, we are again faced with the problem of separating this equilibrium equation into two velocity expressions. It will be convenient, first of all, to try the van't Hoff method, in which it is assumed that only the " free " or " active " molecules react. We have then to put:

$$\frac{dx}{dt} = k \cdot a_A a_B = k \cdot \frac{C_A C_B}{L_A L_B} = k_{obs.} \cdot C_A C_B,$$

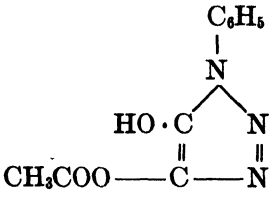
or

$$k_{obs.} = k \cdot \frac{1}{L_A L_B}$$

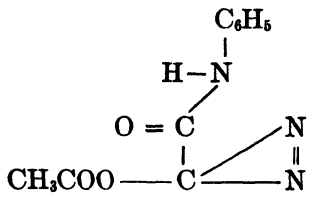
Trautz [200] obtained a similar expression in another way. He combined the equilibrium in the vapor over the solution with that in the liquid through the heat of solution, and derived two velocity expressions from the isochore so obtained. It follows that the velocity in the solution is proportional to the partial pressure of the initial reactants over it, or again proportional to the activity. The observed velocity constants should therefore be inversely proportional to the solubility of the initial reactants

[200] M. Trautz, *Z. physik. Chem.*, 67, 93 (1909).

in any given solvent. Dimroth has carried out experiments on the reaction:



Aciform



Neutral form

of 1 : phenyl 5 : oxytriazole carboxylic ester, in which this view is apparently confirmed. The velocity constants $k_{obs.}$ for 10° C., the solubility of the aci-ester in the respective solvents, and, finally, their product, giving the universal constant k, are shown in the following table for five media, selected from Dimroth's results:

TABLE XXIV — VELOCITY-SOLUBILITY RELATIONS IN VARIOUS SOLVENTS

Solvent	$k_{obs.}$	$L_{(g/liter)}$	$k_{obs.}L = k$
Methyl alcohol	0.00053	218	0.116
Ethyl alcohol	0.00103	97.7	0.101
Acetonitrile	0.0047	41.5	0.195
Chloroform	0.0211	8.8	0.186
Nitrobenzene	0.046	6.5	0.299

The solubilities and the decomposition constants vary in directly opposite fashion and while it is true that the product shows some drift, the variation of the velocity over two powers of ten is practically compensated, in agreement with the requirements of the theory.

Unfortunately, however, this relationship is not so generally valid as would appear from the above example. About the same time,[201] and again later, v. Halban [202, 203] showed that the velocities of decomposition of substituted sulphonium and ammonium salts, which can vary as 1: 300 in different media, are by no means compensated for by the solubility of the substrates. Again, xanthogenic acid is completely miscible with alcohol and carbon disulphide, and yet it decomposes 10^6 times faster in the former. More recently, Eyring and Daniels [204] have carried out more exact measurements of the decomposition of nitrogen pentoxide and find that they do

[201] H. v. Halban, *Z. physik. Chem.*, **67**, 129 (1909).
[202] H. v. Halban, and A. Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).
[203] H. v. Halban, *Z. physik. Chem.*, **84**, 129 (1913).
[204] H. Eyring and F. Daniels, *J. Am. Chem. Soc.*, **52**, 1472 (1930).

not obey the van't Hoff expression. They consider that the medium also has an influence in this case, although small (1:2). This influence should disappear in saturated solution, where the activity is unity (see p. 155) and where the activity of the substrate is alone decisive. The absolute velocity, but not the first order constant derived from the gross concentration, should then be the same throughout. The following values were found however:

TABLE XXV — SOLVENT EFFECT IN N_2O_5 DECOMPOSITION

Solvent	$10^5 \times$ Mol decomposition/liter-sec.
Gas	0.008
Nitromethane	5.92
Carbon tetrachloride	8.75

It is evident that these experimental figures by no means correspond to the required theoretical result.

For reasons such as the above, v. Halban [201, 203] decided to employ a velocity expression different from that of van't Hoff and Dimroth. While this expression is likewise thermodynamically permissible and gives the equilibrium equation, in other respects it is exactly the reverse.

He puts: $$\frac{d[C]}{dt} = k \cdot c_A c_B \cdot L_C \quad \text{or} \quad k_{obs.} = k \cdot L_C,$$

and $$\frac{-d[C]}{dt} = k' \cdot c_C \cdot L_A L_B \quad \text{or} \quad k'_{obs.} = k' \cdot L_A L_B.$$

It is clear that the law of mass action is maintained here in relation to solubility, but now the reaction is accelerated by a high solubility of the end product and not inhibited by a high solubility of the initial reactants. This theory, in which the velocity depends on the properties of the reciprocal system, cannot be so clearly interpreted as the van't Hoff expression. Indeed, Dimroth's results are at variance with the scheme, but it represents v. Halban's own results better.

For instance, in the decomposition of triethylsulphonium bromide:

$$(C_2H_5)_3SBr \rightarrow (C_2H_5)_2S + C_2H_5Br,$$

the velocity varies from 1 to 4 in alcohols, in hydroxyl free bases on the other hand, it varies from 200 to 400. According to v. Halban,[201] this cannot be accounted for by an opposite variation in the solubility of the salt, but only by a variation of the solubility of the decomposition products in the same direction.

v. Halban [228] has directly measured the solubilities of the components in the reaction:

$$O_2N-C_6H_5-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}} + CH_3I \rightarrow \left[O_2N-C_6H_5-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{\overset{+}{N}}}}CH_3 \right] I.$$

He found that the solubilities not only do not compensate for a variation in the velocity of from 1 to 9300, but actually increase it 0.023 to 9300. Accordingly, better agreement is looked for on the basis of the other equation.

It is evident that the influence of the solvent cannot be generally represented by both of these expressions. In pursuance of the reasoning which led us to compare the screening produced by solvation in non-electrolytes to that produced by ions in water, we have now to take into consideration a third possible analysis of the equilibrium expression. This is the Brönsted form (see p. 138) according to which we write:

$$\frac{dx}{dt} = k \cdot c_A c_B \cdot \frac{f_A f_B}{f_{AB}} = k \cdot c_A c_B \cdot \frac{L_{AB}}{L_A L_B}$$

The expression differs from the van't Hoff equation in having the *activity coefficient of the critical complex* in the denominator, or its solubility (if it can be defined) in the numerator. Evidently nothing definite can be said about this new factor. In the case of electrolytes and the salt effect, it is calculably dependent only on the charge, in the first approximation. When we are studying the reduction of activity by solvation, however, specific properties of the molecules as well as of the entirely undeterminable critical complex become of importance. Consequently, any desired effects whatsoever could be ascribed to this unknown factor. Brönsted [187] is not of the opinion, however, that all exceptions to the older formulae can be accounted for by the introduction of the activity coefficients of the X complex. He therefore introduces a medium factor, k_{medium}, independent of the reaction. The assumption achieves some measure of probability since v. Halban's measurements and some old, but fundamental measurements of Menschutkin [205] show that certain solvents generally seem to be " quick " reaction media. With this modification, Brönsted arrives at the expression:

$$\frac{dx}{dt} = k_{\text{reaction}} \cdot k_{\text{medium}} \cdot \frac{f_A f_B}{f_X} \cdot c_A c_B.$$

[205] N. Menschutkin, *Z. physik. Chem.*, 6, 41 (1890).

There are now two unknown factors, and the theory appears to be quite beyond proof. However, there is one point upon which it can be tested, namely that the order of efficiency of the solvents, i.e., k_{medium}, should remain the same in different reactions.

That is by no means true, however. For instance, ammonium salts decompose slowest in alcohols and xanthogenic acid fastest (v. Halban). Menschutkin[206] had already observed similar behavior in several more closely comparable reactions. The formation of ammonium salts from aniline derivatives and halogen alkyls proceeds more rapidly in hydrocarbon solution than the formation of ammonium salts from side chain amines. In acetone, on the other hand, the relations are reversed.

After all, the view that the kinetically active molecules will also be those which are thermodynamically " free " or " active " does not appear to embrace all the known cases, even with the help of special assumptions. It is now generally agreed that besides having a universal influence and besides producing an alteration in the activity (equilibrium), the solvent can still exercise a very specific catalytic effect, in the narrower sense. The variations shown in different solvents have led all investigators to this conclusion.

According to Brönsted, for example, the presence of the solvent produces a new reaction in which the solvent takes part. If cases are excluded in which the latter is used up through such a reaction, which would not be ideal catalysis (compare Eyring and Daniels [207]), the process may be conceived as consisting essentially of a reaction of the solvated molecules occurring with a specific velocity. The process is catalytic in so far as this velocity differs from that of the free molecules. The experiments of Eyring and Daniels [204] are again particularly informative. If the specific velocities of the solvated and free molecules were equal, the velocity constants, that is, the velocity at the same total concentrations, would not differ by 1:2 as observed. Furthermore, the authors were able to deduce from their measurements that the alteration in the velocity with solvation is probably due to a change in the energy of activation and not to a change in the inner vibrational frequency. In most solvents this facilitates the reaction, but in propylene chloride, however, it produces retardation. The effect, therefore, appears to be a genuine example of catalysis and of the " deformation " type, as Bjerrum [109] suggested. The effect can be so pronounced that mutarotation, for example, actually does not take place in many solvents, as we have already seen. On the other hand, it proceeds with considerable velocity in those with amphoteric properties (Lowry [98]).

[206] N. Menschutkin, *Z. physik. Chem.*, **34**, 157 (1900).

[207] H. Eyring and F. Daniels, *J. Am. Chem. Soc.*, **52**, 1486 (1930).

Doubts have also been raised as to how far one can transfer from gas reactions to solution reactions the definitions of a temperature-independent activation energy and a collision number calculable from molecular size and velocity. The papers of LaMer already cited (p. 138) may be indicated in this regard. The comprehensive analysis of bimolecular reactions in solution by Moelwyn-Hughes [207a] leads, however, finally to the conclusion that this method of approach conforms in the main with experimental facts. The deviations that obtain in the direction of velocities higher than calculated signify that more than two degrees of freedom can be carriers of the activation energy (see p. 26). Velocities which are too small perhaps depend on three body collisions, the solvent taking part. In any case it appears at present to be sensible to discuss and compare empirical activation energies.

According to Scheibe, Felger and Rössler [208] the change in the energy of activation by the solvent is to be observed as a displacement $\Delta\nu$ of the maxima of the absorption bands. For two different media this is given by:

$$\frac{k_1}{k_2} = e^{-\frac{h\Delta\nu}{RT}}.$$

However, the change in the energy of activation is not the only effect produced by the medium. It has been shown by Scheibe and co-workers [209] and by Norrish and Smith [210] for the formation of ammonium salts, that the simple equation:

$$k = Z \cdot e^{-q/RT},$$

where Z is the collision number, does not hold in solution, although it was first correctly deduced for the variation in k from a consideration of solution reactions. Scheibe finds that, in calculating the results of Menschutkin and Walden,[211] a different Z must be used for each medium. Likewise, Norrish and Smith find that the collision number for ammonium salt formation in benzene comes out to be 10^8 times less than the figure calculated for the same concentration from gas kinetics. They explain this result by assuming, as Christiansen had done [191] (see also p. 146), that the medium again deactivates the activated molecules by a corresponding amount. However, as the medium must also increase the velocity of activation, this

[207a] E. A. Moelwyn-Hughes, Kinetics of Reaction in Solution, Clarendon Press, Oxford (1933).

[208] G. Scheibe, E. Felger, and G. Rössler, *Ber.*, **60**, 1406 (1927).

[209] G. Scheibe, *loc. cit.*, p. 1418.

[210] R. G. W. Norrish and F. F. P. Smith, *J. Chem. Soc.*, 129 (1928).

[211] P. Walden, *Chem. Ztg.*, **31**, 904 (1907).

theory can only be consistent with the assumption of chain reactions (see p. 172). More recently, Moelwyn-Hughes and Hinshelwood [211a, b] have shown that while many reactions in solution proceed approximately in accordance with the simple collision formula, certain processes, including those mentioned above, are in wide disagreement. In order to decide whether the exceptionally slow rate of the latter is due to deactivation by the solvent as had been suggested, or whether it is a characteristic of the reaction itself, Moelwyn-Hughes and Hinshelwood [211b] investigated the reaction between triethylamine and ethyl iodide in inert or "normal" solvents such as carbon tetrachloride and hexane, and in the gas phase. In all cases, the rate was found to be about 10^8 times slower than that of the hypothetical gas reactions with the observed energies of activation. Similar results were obtained for the reaction between acetic anhydride and ethyl alcohol. It appears, therefore, that the low rate of these reactions is not to be ascribed to deactivation by the solvent, but to some other factor independent of the solvent, and rather that carbon tetrachloride and the hydrocarbons are, to a large extent, catalytically inert.

One obtains the impression, in any case, that the change in velocity in different solvents is brought about by different influences, and, for that reason, a great deal of work is purely empirical. Various empirical investigations have therefore been carried out on the influence of a systematic variation of definite chemical or physical properties of the medium on the reaction velocity.

For instance, Menschutkin [205] found a whole series of constitutive influences on the efficiency of the medium in the formation of ammonium salts, and discovered a striking parallelism with the conductivity (i.e., the dissociation) of hydrochloric acid in the same solvent. This led Nernst [212] to suppose a general connection between the velocity and the "dissociating power" of the solvent, a hypothesis which has much in common with the theory of interacting ions, including its weaknesses. Attempts to relate the dielectric constant of the medium to the reaction velocity possibly arose from this suggestion. The idea was pursued quantitatively by Walden,[211] who found that the velocity of formation of tetraethyl ammonium iodide in 11 media, varying from 1 to 27,000 can be represented by:

$$\sqrt[3]{k_{\text{obs.}}} = \frac{D}{160},$$

[211a] E. A. Moelwyn-Hughes, *Chem. Reviews*, **10**, 241 (1932).
[211b] E. A. Moelwyn-Hughes and C. N. Hinshelwood, *J. Chem. Soc.*, 241 (1932).
[212] W. Nernst, Theoretische Chemie, p. 661. 11–15th Edition, Stuttgart (1926).

hence the " linear velocity " is proportional to the dielectric constant. Similarly, he found an analogous relation:

$$\sqrt[3]{L_c} = \frac{D}{48},$$

to hold for the " linear solubility " of the reaction product (salt). From these equations, it readily follows that:

$$k_{\text{obs.}} = 0.027\ L_c,$$

which is the velocity expression that v. Halban derived from the equilibrium equation, and which we saw applied especially to the formation of ammonium salts (see p. 157). However, Dimroth (loc. cit.) and v. Halban [202] demonstrated that the relation does not hold in the case of other reactions. It would therefore appear to be a property of salt formation.

Another and apparently more successful attempt to connect reaction velocity with the dielectric constant has been made by Harned and Samaras.[212a] They studied the hydrolysis of ethyl orthoformate catalyzed by acetic acid-sodium acetate buffers in various aqueous mixtures of organic solvents. By far the most important catalyst is the hydroxonium ion, to which ethyl orthoformate is extremely sensitive. Accordingly, the process can be regarded for purposes of calculation as a reaction between a neutral molecule and the hydroxonium ion. The change in dielectric constant ($D_1 - D$) and the change in reaction velocity in different media are empirically related by the equation:

$$\log k_0 - \log k = a/b(D_1 - D)$$

where k_0 is the velocity in aqueous solution and k is the velocity in the aqueous mixtures. The value of a/b for mixtures of different organic solvents with water is shown in the following table:

TABLE XXVI — VELOCITY-DIELECTRIC CONSTANT RELATIONS

Solvent admixed	a	b	a/b
Methyl alcohol	0 0565	1.564	0.036
Ethyl alcohol	0.090	2.759	0.033
Acetone	0 105	3.553	0.030
Isopropyl alcohol	0 118	3 977	0.030
n-Propyl alcohol	0 128	4.182	0.031
n-Butyl alcohol	0.171	5.491	0.031

[212a] H. S. Harned and N. Samaras, *J. Am. Chem. Soc.*, **54**, 1 (1932).

Starting from Christiansen's equation (see p. 146) for the velocity in the case of two ions:

$$v = k' c_1 c_2 e^{-\epsilon z_1 z_2 \phi / kT},$$

Harned and Samaras deduce the exponential term from considerations of electrostatics in relation to thermodynamics, for a reaction between an ion and a neutral molecule. Assuming that the change in the rate of orthoacetic ester hydrolysis is due to a "secondary medium effect" on the concentration of hydrogen ions, they show that:

$$ln\, k_0 - ln\, k = ln\, m_{H_0} - ln\, m_H = \frac{\epsilon^2}{D^2 a_i kT}(D_1 - D) = -\frac{2W_e}{kT}$$

where a_i is the ionic radius. Substituting the numerical values:

$$ln\, k_0 - ln\, k = 0.06\ (D_1 - D).$$

The experimental equation is (see above):

$$ln\, k_0 - ln\, k = 0.07\ (D_1 - D).$$

The theory was also shown to be in agreement with the "primary medium effect" in the reaction between methyl iodide and sodium thiosulphate, and in the transformation of substituted chloramino benzenes, although attempts to calculate the hydrogen ion catalysis of ethyl acetate hydrolysis and the hydroxyl ion catalysis of diacetone alcohol on this basis were unsuccessful.

Mention will now be made of Raschig's attempt to bring in the viscosity of the medium.[213] It was based on observations of the inhibition of the decomposition of chloramine by gelatine. However, the example is not very convincing (see p. 170), since Bodenstein [214] was able to show that the same result could be produced by other substances not affecting the viscosity.

A more detailed study of the influence of the viscosity of the medium has been undertaken by Moelwyn-Hughes,[214a] who shows that an extension of Einstein's relation [214b] for the motion of a particle in the Brownian movement leads to the following equation for the collision number in dilute solutions:

$$Z = 2.9 \times 10^{24}\, \sigma\eta / M,$$

where σ is the diameter of the solute molecule, M its mass, and η the viscosity of the solvent. This equation is very similar to one previously

[213] F. Raschig, *Ber.*, **40**, 4588 (1907).
[214] M. Bodenstein, *Z. physik. Chem.*, A **139**, 397 (1928).
[214a] E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 95 (1932).
[214b] A. Einstein, *Z. Elektrochem.*, **14**, 235 (1908).

deduced by Jowett [214c] from a treatment of diffusion. Moelwyn-Hughes concludes, therefore, that the collision rate must be proportional to the viscosity. Proceeding on this basis, he writes:

$$k = \text{constant} \times \eta e^{-E'/RT},$$

since the other terms in Z are approximately independent of temperature. The collision number is therefore governed by the free space and will decrease with temperature.

The following figures were obtained for the decomposition of dibromosuccinic acid in aqueous solution:

TABLE XXVII — VELOCITY-VISCOSITY RELATIONS

$T°$	$\eta \times 10^3$	Unimolec. velocity consts. secs.$^{-1}$	
		obs.	calc.
15	11.4	$1\ 61\ 10^{-7}$	$7.75\ 10^{-7}$
40	6.57	$1\ 41\ 10^{-6}$	$1.41\ 10^{-5}$
80	3 56	$7.67\ 10^{-5}$	$7.30\ 10^{-4}$
101	2.81	$5.30\ 10^{-4}$	$4.28\ 10^{-3}$

It is evident that the reaction velocity approximates to that given by a simple collision mechanism of activation, without exceeding it, however. Similar results were obtained for certain other unimolecular reactions.

A very promising method of investigation has been used in work by Grimm and Ruf. [215, 215a] Instead of varying the medium in an aimless manner, they employ solvents of analogous constitution, and Z and q moreover, are measured simultaneously. Experiments were carried out in hydrocarbons, halobenzenes, nitro derivatives, and aromatic ethers.

The value of the energy of activation for the formation of tetraethyl ammonium iodide was approximately the same (12.0 ± 0.5 kilocals.) in all cases, except in the two hydrocarbons C_6H_{12} and C_6H_{14}. In the halobenzenes, the Z values were in the order:

$$H < F < Cl < Br,$$

that is, in the order of the atomic radii of the substituents, or of the molecular magnitude of the solvent. It is clear that the Z values in this reaction are influenced by some related property of the medium without any essential influence on q.

Furthermore, solvents such as nitrobenzene and cyanobenzene, possess-

[214c] M. Jowett, *Phil. Mag.*, **8**, 1059 (1929).

[215] H. G. Grimm and H. Ruf, *Reunion Intern. de Chim. Phys.*, p. 205, Paris (1928).

[215a] H. G. Grimm, H. Ruf, and H. Wolff, *Z. physik. Chem.*, B **13**, 301 (1931).

ing dipole moments (high dielectric constants) show considerably higher (30 times) Z-values. It is uncertain, however, which of these effects represent alterations in the activity and which represent changes in the collision number or collision yield, since the solubilities were not determined. The constancy of the apparent activation energies, q, would indicate reasonably comparable or small heats of solution. This work nevertheless indicates that such a systematic variation of the properties of the medium leads to progress.

A similarly planned systematic variation of the reaction studied is also necessary for, as we have seen, a whole series of possibilities exist in which the medium can influence a reaction and that, probably, the different possibilities are not the same for all reactions. Possibly the formation of ammonium salts is not a very typical example of the reactions of organic neutral molecules. It is only by experimental investigations extended systematically in this direction that one can hope to distinguish the various influences of the solvent which at present seem so inseparable.

It is precisely in this direction that the greatest experimental and theoretical activity has been manifested in the last two years. The development of the concept of activation energy in terms of a potential energy barrier over which the reactants pass in their change to reaction products has led to the formulation, in the special case of three hydrogen atoms, by Pelzer and Wigner,[215b] and quite generally by Eyring,[215c] of the absolute velocity of chemical reactions as a function of the concentration of the "activated complex" or "transition state."[215d] This activated complex represents the position of maximum potential energy or minimum probability in the configuration of the atomic system as it passes from initial to final state or *vice versa*. The concentration of the activated complex in a given set of conditions or, as Evans and Polanyi express it, the population of the transition state can be determined by statistical mechanical methods. The average life of the activated state can be expressed in terms of a distance dl along the potential surface reaction path divided by the velocity v with which the system is changing. As Eyring has pointed out this average life will normally have a value approximately $\frac{kT}{h}$.

Wynne-Jones and Eyring[215e] have shown how this concept of the abso-

[215b] Pelzer and E. Wigner, *Z. physik. Chem.*, B **15**, 445 (1932).
[215c] H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).
[215d] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).
[215e] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

lute rate of reaction can be applied to processes occurring in condensed phases. It is shown that reactions may occur either more slowly, faster or at the speeds calculable on collision mechanisms of reaction and that the velocity, whether fast, slow or normal is determined by the properties of the activated complex. Evans and Polanyi [215d] applied the concept to the interpretation of the effect of pressure on reactions in solutions. Their considerations indicate that in an association reaction A + B = AB, which is generally accompanied by a reduction in volume, the association should be accelerated and the dissociation impeded by hydrostatic pressure. Experiments of Perrin, Gibson and Williams [215f] on the reaction benzylmethylaniline and allyl bromide to give the corresponding ammonium bromide fully confirm the conclusions from theory.

Wynne-Jones and Eyring emphasize that previous theories of reaction rate such as that of Brönsted are special cases of the general theory of reaction rates now developing, which reduces the problems of kinetics to the thermodynamic calculation of an equilibrium constant for the activated complex and the calculation of a transmission coefficient. They point out that the principal problems are those met in calculating an entropy and a heat of reaction, and that kinetic difficulties disappear when viewed in the light of this theory. Polanyi [215g] and Hinshelwood [215h] have recently discussed the advantages of each method of approach.

[215f] Perrin, Gibson and Williams, *Proc. Roy. Soc.*, A **154**, 684 (1936).
[215g] M. Polanyi, *J. Chem. Soc.*, 629 (1937).
[215h] C. N. Hinshelwood, *J. Chem. Soc.*, 635 (1937).

CHAPTER IX

NEGATIVE CATALYSIS IN SOLUTION

THE first quantitative observations of the retardation or negative catalysis (also called "paralysis" and "inhibition") of a reaction, by apparently indifferent substances present in the solution, were made by Bigelow [216] in 1898. He studied the oxidation of sulphites by atmospheric oxygen and established that all possible additions of organic material containing hydroxyl groups strongly retard the formation of sulphate. Since he had found the reaction to be very much dependent on the previous history of the water employed, he could not draw any very precise conclusions. Nevertheless, he was able to establish that the half-lives were about proportional to the concentrations of the added material, and that the order of negative catalytic efficiency is roughly as follows: benzyl alcohol, β butyl alcohol, allyl alcohol, *i*-butyl alcohol, *n*-butyl alcohol, propyl alcohol, ethyl alcohol, mannite, ethylene glycol, methyl alcohol, glycerine, tert-butyl alcohol.

Later, these researches were taken up again by Titoff [217] who confirmed the essential results. He also succeeded in clearing up the problem of the great sensitivity of the sulphite oxidation to the quality of the water, by showing that traces of iron and, more particularly, of copper, which is difficult to exclude, act as positive catalysts. One gram of copper in 16 million litres of solution accelerates the reaction 30 per cent. Consequently, he afterwards worked with solutions of known copper content and so obtained reproducible data. Numerous experiments with mannite as the retarding agent showed that 1800 mols are required to compensate for the effect of one mol of cupric ion, and that the velocity decreases rather more rapidly than the reciprocal of the mannite concentration. Tin salts, ammonium salts, and potassium cyanide retard to a still greater extent, referred to copper.

While we have regarded positive catalysis as providing a new course for the reaction (see p. 13), it is clear that a similar conception cannot hold for negative catalysis, since there is no reason why the reaction should take the new, slow course, in preference to the easier, old one. Therefore, every

[216] S. L. Bigelow, *Z. physik. Chem.*, **26**, 493 (1898).
[217] A. Titoff, *Z. physik. Chem.*, **45**, 641 (1903).

theory which is advanced to explain the phenomenon must proceed on the basis that the inhibitor intervenes at some stage in the original course of reaction, making it more difficult or impracticable. From the standpoint of the theory of intermediate reactions, it can be assumed that some particular link in the reaction, whether it be a catalyst, or one of the reactants, or an intermediate, is wholly or partly removed by the formation of an inert compound.

Titoff's experiments, particularly in regard to the sensitivity of the reaction to copper, led him and Luther [218] automatically to the original assumption that the negative catalyst removes a positive catalyst. Copper is certainly known to enter into many complexes with organic oxy-compounds. Titoff accordingly assumed that the non-inhibited reaction proceeds in accordance with the equation:

$$\frac{dx}{dt} = k[\mathrm{Cu}^{\bullet\bullet}] \cdot [\mathrm{SO_3}''],$$

and, on the other hand, that cupric ions react with the inhibitor, Inh:

$$\mathrm{Cu}^{\bullet\bullet} + \mathrm{Inh} \rightleftarrows [\mathrm{Cu\ Inh}^{\bullet\bullet}].$$

The concentration of $\mathrm{Cu}^{\bullet\bullet}$ is then:

$$[\mathrm{Cu}^{\bullet\bullet}] = [\mathrm{Cu}^{\bullet\bullet}]_{\mathrm{Comb.}} \quad K/[\mathrm{Inh}].$$

K is the dissociation constant of the complex, assumed to be small in comparison with [Inh], while it is further presumed that $[\mathrm{Inh}] \gg [\mathrm{Cu\ Inh}^{\bullet\bullet}]$. It follows therefore, that:

$$\frac{dx}{dt} = \frac{Kk[\mathrm{Cu}^{\bullet\bullet}]_{\mathrm{Comb.}}\,[\mathrm{SO_3}'']}{[\mathrm{Inh}]}.$$

The inverse dependence of the velocity on the concentration of mannite could be explained in this way, and, when the complex contains more than one molecule of mannite, the inverse dependence may even be greater than hyperbolic. Luther explained the effect of the tin salts by the adsorption of the cupric ion on stannic oxide, analogous to the formation of lakes. These processes compete with the reactions:

$$3\mathrm{SO_3}'' + 2\mathrm{Cu}^{\bullet\bullet} + \mathrm{H_2O} = \mathrm{SO_4}'' + 2(\mathrm{Cu^I SO_3})' + 2\mathrm{H}^{\bullet} \quad \left\{\begin{array}{l}\text{measurably}\\ \text{slow,}\end{array}\right.$$

$$2(\mathrm{Cu^I SO_3})' + 2\mathrm{H}^{\bullet} + 1.5\mathrm{O_2} = 2\mathrm{SO_4}'' + 2\mathrm{Cu}^{\bullet\bullet} + \mathrm{H_2O} \quad \left\{\begin{array}{l}\text{extremely}\\ \text{rapid,}\end{array}\right.$$

$$\text{Total: } 3\mathrm{SO_3}'' + 1.5\mathrm{O_2} = 3\mathrm{SO_4}'',$$

which promote the change (see, however, p. 176).

[218] R. Luther, *Z. angew. Chem.*, **19**, 2049 (1906).

It will soon be apparent that the theory has been inopportunely applied here. Nevertheless, in many cases, the principle is still very useful, and Bäckström's statement [219] that apart from the secondary salt effect there are practically no such examples of the removal of a positive catalyst by a negative catalyst, is not altogether correct.

The decomposition of ethylene iodide into ethylene and iodine, catalyzed by iodide ions, has been studied by Slator.[220] He established that the catalysis is inhibited by all substances which form complexes with the iodide ions, for example, I_2, HgI_2, and $Cd^{\cdot\cdot}$. According to Bredig and Walton,[114] the iodide ion catalysis of the decomposition of hydrogen peroxide is also inhibited by the same substances. The fact that, properly speaking, this is an iodine-iodide ion catalysis (see p. 80), naturally does not affect the significance of the observations in the least. In particular, the cases discussed on pp. 93, 98, should be included here, reactions in which acid catalysis in alcohol is inhibited by water, through the latter competing with the alcohol for the acid or hydrogen ions (esterification, Goldschmidt, [133] decomposition of diazoacetic ester, Bredig [139, 144]). Lowry [98] has shown that mutarotation in chloroform (see p. 121) is stopped by the production of phosgene which removes basic catalysts by the formation of carbamides. Likewise, according to Bodenstein,[214] the inhibition of the decomposition of chloramine by gelatine and similar substances (see p. 164), observed by Raschig,[213] can be attributed to a complex of the catalyzing copper.

In the case of reactions which occur without the aid of catalysts, however, another theory has to be employed. The simplest assumption is that the reactive form or active intermediate state of one of the reactants or of an intermediate compound is removed by the negative catalyst. Bredig and Lichty [221] observed that the decomposition of oxalic acid into carbon monoxide and carbon dioxide in concentrated sulphuric acid, is very strongly inhibited by water in accordance with the expression:

$$k = \frac{k_0}{[H_2O]^2}$$

They consider that an intermediate, which may be an anhydride of oxalic acid ($\begin{matrix} CO \\ | \quad \diagdown O \\ (CO \quad \diagup \end{matrix}$), an intermediate compound of both acids, or, according to Christiansen,[222] SO_3, combines with two molecules of water and is removed from the reaction.

[219] H. J. L. Bäckström, *Trans. Faraday Soc.*, **24**, 706 (1928).
[220] A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).
[221] Bredig and D. Lichty, *Z. Electrochem.*, **12**, 460 (1906).
[222] J. Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

This kind of explanation was also advanced by Moureu and Dufraisse [95] to account for their extremely interesting observations on " anti-oxygens." They found that the autoxidation of aldehydes and of unsaturated compounds in air can be completely stopped by the addition of extremely small amounts of other oxidizable substances, particularly phenols. The theory is closely connected with the conception which we adopted for the process of combustion (see p. 65). It was presumed that the inhibition of autoxidation consists in the production of molecular oxygen from intermediate peroxides or moloxides, analogous to the interaction of two higher oxides to give two lower oxides and oxygen:

$$H_2O_2 + MnO_2 \rightarrow H_2O + MnO + O_2.$$

The autoxidation process might occur according to the following scheme (see p. 65), the oxygen in parenthesis signifying loosely bound, active oxygen:

$$A + O_2 \rightarrow A(O_2),$$
$$A(O_2) + A \rightarrow 2A(O) \rightarrow 2AO.$$

The antioxygen B now intervenes in accordance with:

$$A + O_2 \rightarrow A(O_2),$$
$$A(O_2) + B \rightarrow A(O) + B(O) \rightarrow (A + B + O_2?),$$

or thus:

$$A + O_2 \rightarrow A(O_2),$$
$$A(O_2) + B \rightarrow A + B(O_2),$$
$$A(O_2) + B(O_2) \rightarrow A + B + 2O_2(?).$$

The interesting observation that autoxidation can be inhibited or accelerated by the same substance according to the conditions, as, for example, by pyrogallol in the aging of rubber (Moureu [223]), can be explained by the following mechanism:

$$A + O_2 \rightarrow A(O_2),$$
$$A(O_2) + B \rightarrow A(O) + B(O)$$

acceleration: $B(O) + A \rightarrow A(O) + B$

inhibition: $A(O) + B(O) \rightarrow A + B + O_2$

This agrees with the view that the primary active intermediate is removed by the added substance.

We must also consider here a number of other theories of negative catalysis which have been proposed, and which are based on the view that the

[223] H. Moureu, *Trans. Faraday Soc.*, **24**, 708 (1928).

added substance is able to deactivate excited molecules that would normally react in virtue of their high energy of activation. We have seen, for instance, that Norrish and Smith [210] explained the apparent inhibitory effects of solvents in this way. Christiansen [191] assumed deactivation of the collision complex by ions of the environment in ionic reactions. It has already been indicated, however, that these theories encounter a difficulty when employed in their simplest form. The energy transference from the activated substrate molecule to the negative catalyst must be reversible; otherwise the catalyst would displace the Maxwellian activation equilibrium. Consequently, the added substance must increase the velocity of activation to the same extent as the velocity of deactivation. If the active product is an Arrhenius intermediate, that is, the velocity is determined by the subsequent reaction, the catalyst produces no alteration in the rate, since the concentration of the intermediate is unchanged. If the intermediate is of the van't Hoff type, however, the velocity of activation is decisive and the reaction can be greatly accelerated.

The same objection applies to the mechanism of antioxygens, just described, in which the last step produces $A + B + O_2$. This would mean that B displaces the activation equilibrium $A + O_2 \rightarrow A(O_2)$ without being consumed. We saw on p. 14 that this cannot be accomplished by an ideal catalyst which is not used up in the reaction. On the other hand, the antioxygens were actually consumed only with extreme slowness.

Therefore, in order to have negative catalysis by deactivation, it is necessary to bring in an assumption upon which we have already relied in the treatment of negative gas catalysis (see p. 56), namely the occurrence of reaction chains which are broken by the negative catalyst.

A further reason in support of this view, is that it is only by such an assumption that the extraordinary small quantities of negative catalysts effective in the experiments of Titoff and of Moureu and Dufraisse can be accounted for satisfactorily. H. S. Taylor [224] had suggested a possible explanation without the assumption of chains, according to which the activated molecules are captured by the negative catalyst. He showed that in the experiments of Moureu and Dufraisse, the number of benzaldehyde molecules reacting per minute in the non-inhibited process is approximately equal to the number of molecules of hydroquinone inhibitor present in the inhibited reaction. He compared the negative catalyst to an attendant among 100 lunatics (the " lunatics " are the molecules of the substrate; when activated, they become violent). " The warden would be powerless were all the lunatics simultaneously violent. Only at intervals does an oc-

[224] H. S. Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

casional lunatic become a candidate for a padded cell. The warden cares for him, the gentler 99 do not require attention." Christiansen [222] remarks, however, that this would be crediting the catalyst with too much intelligence.

We are indebted to Bäckström [225, 226] for a direct demonstration of the chain character of the processes studied by Moureu and by Titoff. He showed first of all [225] that the autoxidation of aldehydes (benzaldehyde and oenanthaldehyde) in light has a quantum yield of several thousand. A similar result was obtained in the case of sodium sulphite. Furthermore, the quantum yield is reduced by the addition of inhibitors, e.g., in one case, mannite reduced the quantum yield of the sulphite reaction from 40,000 to 13,000. The substances that inhibit the photochemical chain are the same as those which inhibit the dark reaction and in many cases produce an identical reduction. It can be concluded, therefore, that the dark reaction is also a chain process and that similar rules apply here as were found in the case of gaseous reactions (p. 56). Actually, the velocities of the dark reaction both for oenanthaldehyde and sulphite autoxidation obey the equation:

$$v_d = \frac{k[\mathrm{A}]}{k_1[\mathrm{A}] + k'[\mathrm{Inh}]}$$

which is of the form to be expected for the inhibition of a chain reaction. k and k' are to be considered as being made up of a combination of velocity constants and oxygen concentration. When the sulphite concentration is constant, the equation becomes:

$$v_d = \frac{k}{k_1 - [\mathrm{Inh}]}.$$

It was found that the same equations hold for the photochemical reaction, with the same inhibition constants k'. Hence we have:

$$v_l = k'' v_d.$$

Later,[226] the results on sulphite oxidation were still further elaborated. It is to be expected that the chains are broken through the alcohols themselves being oxidized, especially since Bigelow [216] had found tertiary butyl alcohol to be ineffective. This could be directly established by careful identification of the aldehydes and ketones formed. Again, if the reaction velocity (formation of sulphate) is given by:

$$v_d = \frac{k[\mathrm{A}]}{k_1[\mathrm{A}] + k'[\mathrm{Inh}]},$$

[225] H. L. J. Bäckström, *J. Am. Chem. Soc.*, **49**, 1460 (1927).

[226] H. L. J. Bäckström, *Trans. Faraday Soc.*, **24**, 601 (1928); *Medd. Nobel-Inst.*, **6**, Nr. 15 and 16 (1927).

the probability that a chain will be broken by a molecule of alcohol is:

$$\frac{k'[\text{Inh}]}{k_1[\text{A}] + k'[\text{Inh}]},$$

and when n chains are terminated in unit time, the velocity of oxidation of the alcohol is:

$$\frac{-d[\text{Inh}]}{dt} = \frac{nk'[\text{Inh}]}{k_1[\text{A}] + k'[\text{Inh}]} = \frac{nk'[\text{Inh}]}{k[\text{A}]} \cdot v_d.$$

Therefore, when [A] is constant, [Inh] v_d is proportional to the velocity of oxidation of the alcohol, $-d[\text{Inh}]/dt$.

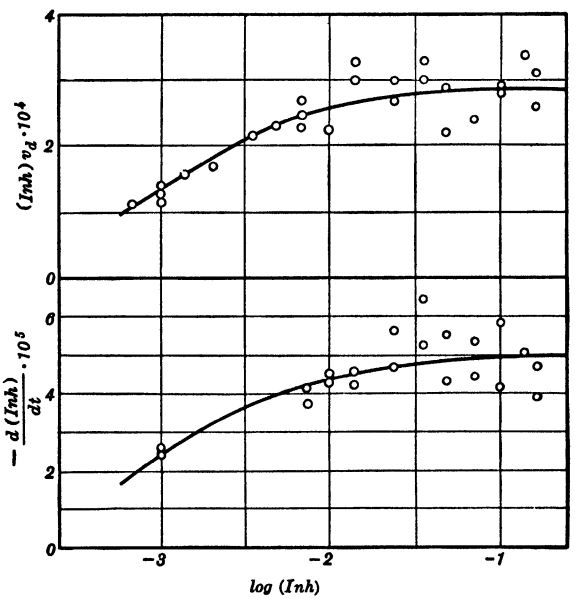


FIG. 23. Inhibition of the Autoxidation of Sulphites by Benzyl Alcohol. The Upper Curve Shows the Velocity of Oxidation of the Alcohol According to the Chain Theory; the Lower, by Analysis (Bäckström).

Alyea and Bäckström have determined [Inh] $\cdot v_d$ separately, and obtained $-d[\text{Inh}]/dt$ by colorimetric determinations of the oxidation products. Fig. 23 shows that both values have the same dependence on [Inh] as demanded by the equation. In the diagram, log[Inh] is measured as abscissae.

With large alcohol concentrations, the number of chains broken ($-d[\text{Inh}]/dt$) becomes independent of the alcohol concentration, since they are *all* broken under these conditions. In this constant region, the velocities of induced oxidation of different alcohols become partially identical, as ap-

pears from the accompanying table of data from the work of Alyea and Bäckström.[226a]

TABLE XXVIII — INHIBITION BY ALCOHOLS

Alcohol	Alcohol concn. where constant velocity obtains	Average $[\text{Inh}] \cdot v_d$	k' from $[\text{Inh}] \cdot v_d$	$\frac{d[\text{Inh}]}{dt}$	Chain length
Isopropyl-	0.05–1.5	0.0034	3 0	0 000046	740
Butyl	0 15–1.8	0.0103	1	0 000049	2100
Benzyl	0.0073–0.167	0.00028	37	0.000048	58

All three alcohols were oxidized with equal rapidity in the constant region, despite widely different inhibitory powers. The mean chain length is given in the last column. In the constant region this is obviously equal to:

$$[\text{Inh}] \cdot v_d : d[\text{Inh}]/dt.$$

It is of course greatest for the least efficient inhibitors.

The best evidence for the correctness of the theory lies in the fact that identical values were obtained for the chain length by direct photochemical determination of the quantum yield; for example, the average chain length for benzyl alcohol was found to be 64 links, instead of the value 58 found above. It appears, therefore, that all chains have the same probability of ending in the oxidation of a molecule of alcohol, independently of whether the first step in the chains was initiated by thermal or photochemical means.

A detailed investigation of the inhibition of the oxidation of benzaldehyde by anthracene was later reported by Bäckström and Beatty.[226b] They conclude that the chain is broken by reaction of the anthracene with an active form of the peroxide to give anthranol, since anthracene is unaffected by benzo-peracid itself. It is shown that the deactivation of the active peroxide is rather a specific process, the collisions with anthracene being at least 1000 times more efficient than the collisions with benzaldehyde. However, Bäckström does not consider this to be the only possible inhibitory process and attributes the slightly negative catalytic effect of benzoperacid to deactivation of the primarily excited molecules of aldehyde.

Returning to the rôle of copper in autoxidation processes, which was of such importance in the old theory, Alyea and Bäckström [226a] were able to show that it only increases the number of chains without having any influ-

[226a] H. N. Alyea and H. J. L. Bäckström, *J. Am. Chem. Soc.*, **51**, 90 (1929).
[226b] H. L. J. Bäckström and H. A. Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

ence on chain breaking. According to Haber and Franck,[226c and d] the rôle of copper in the autoxidation of sulphite is to produce radicals which then propagate the chain. Baubigny [226e] had shown that in the absence of atmospheric oxygen, cupric salts and alkali sulphites form dithionates. Haber and Franck propose that this takes place through the formation of the " radical " monothionic acid HSO_3 by reduction of the copper:

$$SO_3'' + Cu^{\bullet\bullet} = SO_3' + Cu^{\bullet}.$$

In the absence of atmospheric oxygen, HSO_3 very rapidly dimerizes to dithionic acid, and, for that reason, cannot itself be isolated, but, in presence of oxygen, it is presumed to react as follows:

$$HSO_3 + O_2 + SO_3'' + H_2O = 2SO_4'' + OH + 2H^{\bullet}.$$

This may be imagined as a triple collision in presence of water, or as two successive reactions through HSO_5. The chain reaction now proceeds according to:

$$SO_3'' + OH = SO_3' + OH',$$

and back to

$$SO_3' + H^{\bullet} = SO_3H.$$

Haber [226c] considers that the catalytic effect of the heavy metals in autoxidation processes generally, is to be attributed to the production of radicals.

The precise rôle of the inhibitor in such mechanisms becomes extremely problematical, although the actual chain character of the Titoff and the Moureu reactions may now be taken as well established. We have, moreover, met with a number of negative catalytic processes which do not fall into line with those investigated by Bäckström and which for the time being may therefore be considered from the point of view of the old theory.

[226c] F. Haber, *Naturwiss.*, **19**, 450 (1931).
[226d] J. Franck and F. Haber, *Sitzber. preuss. Akad. Wiss. Phy-math. Kl.*, 250 (1931).
[226e] H. Baubigny, *Compt. rendu.*, **154**, 701 (1912); *Ann. de Chim. Phys.*, **1**, 201 (1914).

CHAPTER X

HETEROGENEOUS CATALYSIS

General Introduction

It is a well-known fact that the majority of all catalytic reactions, with possibly the partial exception of those occurring in organisms, do not belong to the types hitherto discussed, but are heterogeneous catalyses. By this we mean catalytic processes in a heterogeneous system, not in the sense that some one phase or other of such a system contains substrate and catalyst (homogeneous catalysis), but that catalyst and substrate are now to be found in two different phases. The reaction naturally takes place, at least in so far as it is catalytic, only at the phase boundary, at the two dimensional surface bounding the two three dimensional phases. The important distinction of this type as compared with homogeneous catalysis lies in this fact of the localization of the chemistry of the process and questions arise which in homogeneous catalysis are quite pointless, such as the structure of the surface and the distribution of its active areas, the modification and change of the surface by the reaction occurring, in other words, topochemical problems; and these have to be considered in addition to the old and basic problems of catalysis.

It might, therefore, be asked why such new problems are undertaken and a study of heterogeneous catalysis made before such fundamentals are solved. Concerning this, on the one hand, it may be said that we are sufficiently well informed about certain basic factors of reaction kinetics that, assuming these, we are in a position to undertake the special problems of heterogeneous processes. On the other hand, the importance of biological processes and the increasing technical application of heterogeneous catalytic processes compel us, even now, to investigate such processes scientifically.

The fact that heterogeneous catalytic reactions are so numerous in industry and in the world of organisms is involved in the nature of these processes. There are, naturally, very many more possibilities for the encounter of two molecular species, substrate and catalyst, when the additional requirements of mutual solubility or co-existence in the gas phase or common solubility in a solvent are unnecessary.

At first glance it seems hard to understand how the presence of a catalyst in one phase can in any way influence the velocity of reaction in the other phase. An analogy, which Bredig [227] has used, helps to an understanding of this. Let us think of a reactant A dissolved in a solvent I in which the velocity of reaction is very small. This solvent is in contact with another solvent, II, in which the velocity of change $A \rightarrow B$ is considerable. An example, experimentally verified by Hughes,[228] may be cited: A = $AgNO_3$ + HCl, I = Ether, II = Water. The distribution equilibrium of A between I and II will be established or can be considered as established. The system A in solvent II rapidly reacts there to form B, whence, by establishment of its distribution equilibrium, there results a transformation from A in solvent I to B in the same solvent. The requirement for acceleration of the process is that, of the successive steps, (1) diffusion of A from I to II, (2) reaction in II, and (3) diffusion of B from II to I, each, singly, must occur more rapidly than the conversion in I itself. It can further be seen that the reaction need not occur in the whole phase II but needs only to penetrate into the surface layer in order to yield the desired effect. With solid catalysts this will be the preferred mechanism. We, therefore, reach the conclusion: *The surface of a heterogeneous catalyst is a seat of enhanced reaction velocity.* Whether this velocity can, in the last analysis, actually be measured, or whether it will be obscured by the preliminary or subsequent diffusion processes owing to their slower tempo is a special question which must be decided in individual cases, and which will later be specially discussed (see page 221).

If, now, the question be asked as to why the reaction velocity at the interface is greater than in solvent I, we can connect the case under consideration with the discussion that has already been given concerning the influence of the solvent (page 154). It was there shown that such an effect was not attainable through a change in velocity with the activity (referred to unit activity for saturated solutions). Rather it was to be expected that velocities would be equal in solutions which were in equilibrium with one another if, in the media in question, the reaction occurred between molecules, which we there named " free " molecules (page 158).

To explain the large deviations from this requirement which were found it was concluded that there is present a " specific catalytic " action of the medium; that, therefore, molecules on which the solvent exercises special forces react rapidly. The same must be true in our present case, for, if II

[227] G. Bredig, Habilitationsschrift, Leipzig, 1901, p. 92. See W. Ostwald, *Physik. Z.*, 3, 313 (1902).

[228] R. E. Hughes, *Phil. Mag.*, 35, 531 (1893).

is in equilibrium with I and we yet observe a greater absolute velocity in II, the influence of a somewhat different solubility is excluded and there must be present a specific interaction, a " deformation-catalysis " (Bjerrum). We thus come to our second point: *The acceleration of reaction in the surface results from forces of the catalyst acting on the substrate molecules, from a deformation of one kind or another.*

If again we transfer our discussion from the reaction within the solvent II to the surface reaction at a solid contact agent, we must likewise ascribe a change of state to the substrate molecules, " dissolved " in, that is to say " adsorbed " at, the surface. Catalytically active adsorption must, therefore, produce a deformation, considering this for the time being in its widest possible sense. For adsorption which fulfills this condition it has been proposed to assign a special name " Chemosorption," but no sharp limits can be drawn.[229] The particular nature of the influence which the catalyst exercises on the substrate molecules will be discussed in special cases later (see page 234).

We can classify heterogeneous catalytic reactions according to the state of aggregation of the phases in contact with one another. The following combinations thus result:

I Substrate gaseous; Catalyst liquid.
II Substrate gaseous; Catalyst solid.
III Substrate liquid; Catalyst gaseous.
IV Substrate liquid; Catalyst liquid.
V Substrate liquid; Catalyst solid.
VI Substrate solid; Catalyst gaseous.
VII Substrate solid; Catalyst liquid.
VIII Substrate solid; Catalyst solid.

It may first be noted that Types III, VI and VII are, in practice, much less numerous than the others. Sauter [229] rightly points out that these are the cases in which the catalyst possesses the less dense state of aggregation. Consequently, the unsaturated forces at their surfaces are always smaller and, as a consequence, the adsorption activity towards the substrate is less. Still, this is only useful as an orientation to the statistical analysis of catalytic reactions; reactions of these rare types are known.

The most numerous catalytic processes, by far, are gaseous reactions and reactions in solution occurring at solid surfaces. Since reactions in solution suffer from numerous complications due both to adsorption and ac-

[229] See, for example, E. Sauter, *Kolloid Z.*, **46**, 148 (1928); **49**, 450 (1929); *Z. Elektrochem.*, **36**, 874 (1930); *Heterogene Katalyse*, Leipzig and Dresden 1930.

tivity, we shall mainly treat, as the prototype of heterogeneous catalytic reactions, gas reactions occurring at solid surfaces (Type II) and shall discuss reactions in solutions (Type V) only occasionally in the better understood cases. Other possibilities, especially the important Type VIII, we shall discuss in the concluding sections.

When we consider gas reactions occurring at solid surfaces (Type II) it is their wide distribution which is first of all so noticeable. According to a summary of Bodenstein [230] practically all measurements of homogeneous gas reactions are sensitive to influences of the walls of the containing vessel, that is, to heterogeneous catalysis. This catalysis can be both an acceleration and an inhibition. In many reactions, especially decomposition processes (e.g., PH_3), a side reaction takes place at the wall, often occurring even orders of magnitude faster than the homogeneous reaction. On the other hand, the wall may exercise a negative or inhibitive influence, especially in chain reactions, where the wall is in a position to break chains. We have already touched upon this effect in a preliminary manner (page 54), but we shall return to its discussion in greater detail later, as well as to the recently discovered capacity of the walls even to start reaction chains.

[230] M. Bodenstein, *Z. Elektrochem.*, **35**, 535 (1929).

CHAPTER XI

ADSORPTION

THE surface of the solid catalyst in a gaseous system has been identified as the seat of catalytic action; adsorption at the surface has been recognized as the essential preliminary to an attack on the substrate. In heterogeneous catalysis, we are confronted with a new situation, that is, to consider separately that portion of the substrate which is adsorbed and, therefore, is alone in a position to react. A discussion of heterogeneous reactions must, therefore, be preceded by a consideration of adsorption both as to type and magnitude.

The forces which hold together the denser phase of the catalyst (adsorbent) are van der Waals forces in liquids and in molecular lattices; in ionic lattices they are electrostatic forces, in atomic lattices homopolar bonds, and in metallic lattices the allied forces of "metallic bonding." At the surface, all these forces cause a unidirectional attraction inwards which operates to produce a diminution of the surface, the surface tension. The product of the surface tension and the surface area is the free surface energy. Equilibrium is attained when the free energy, and, therefore, the free surface energy, is a minimum. Every process which lowers the surface tension will, therefore, occur spontaneously so long as it continues to produce such a lowering.

Such a diminution is possible when suitable molecules from the surrounding gas phase (or solution) saturate the free forces of the adsorbent at its surface, in that they are bound to the surface by electrostatic, homopolar or dipole forces of attraction, are bound, therefore, either chemically or physically. The cause of the adsorption lies, thus, in the binding energies which the unit elements of the adsorbent exert on the molecules of the substance to be adsorbed.[230a]

The picture obtained by a glance at the field of adsorption phenomena is by no means so clear and precise as that obtaining in the case of homogene-

[230a] Dr. Schwab employs the German word "Adsorptiv" for the substance to be adsorbed and the word "Adsorbat" for the surface compound formed, pointing out, at the same time, that this latter term (in English, the adsorbate) has been employed, somewhat incorrectly linguistically, to designate the adsorbed substance itself. The use of the word adsorbate with this latter significance has become frequent in English recently. Tr.

ous solutions. This arises on the one hand because, as already pointed out, the nature of the forces operating on the adsorbed substance may be very varied; as a consequence, the substances adsorbed and the magnitude of their adsorption may show great variations. On the other hand, the magnitude of the forces acting, that is to say the surface tension, is by no means uniform over the whole surface in the case of solid adsorbents; we shall, in the following pages, continuously meet this fact of the presence of " active centers," a factor of extreme importance in catalysis. Thirdly, there is a complicating factor which lies in the nature of the adsorbed substance itself, the fact that these molecules exert attractive forces on each other, as in the case of liquids, in which they also come into close contact with one another. Hence, it follows that the surface, even when it is completely covered with a layer of adsorbate molecules, has often not attained its minimum surface tension, since the outward attractive forces of the adsorbed molecules for molecules of their own kind are not completely saturated. Hence, therefore, a second layer will be adsorbed, with, however, diminished energy, then a third and so on until the attractive forces are reduced to negligible proportions.

Capillary Condensation: If the gas pressure is smaller than the saturated vapor pressure, at the same temperature, of the liquid form of the material that is being adsorbed, the adsorption process reaches an equilibrium. If it is greater than the saturated vapor pressure the process finally goes over into a condensation of the free liquid. We see, therefore, that, through the forces of the adsorbent, a kind of condensation can be attained at pressures below the vapor pressure and limited to the surface layer. This effect is especially pronounced if the adsorbent has a very extended surface, with many pores, passages and capillary spaces since, thereby, many molecules can be brought under the influence of the more extensive van der Waals sphere of action of the adsorbent. This is the typical case of adsorption that is observed, for example, with adsorption charcoal and silica gel, both having very extended surfaces. For such, the rule holds that the most readily condensible substances (high critical temperature) are also the most strongly adsorbed. This arises because the attractive forces between the solvent molecules themselves are the greatest. On the other hand, it is also understandable that a certain selectivity on the part of the adsorbent arises by reason of the variation of its own primary forces of attraction. We can designate such adsorption with the name " Capillary condensation " without thereby wishing to imply that the condensation occurs in all cases only in the capillary pores and does not occur on the plane surfaces. In any case, it is striking that the adsorption can be annihilated by a

smoothing of the surface through strong heating or chemical treatment (for example with nitrous oxide).[231]

With this type of adsorption many investigators have been concerned both theoretically and experimentally. We may cite here Magnus,[232] and Polanyi,[233] and the comprehensive summaries by Hückel,[234] Cassel,[235] Jaquet [236] and McBain.[236a]

All these theories share this in common that they associate the magnitude of the adsorption and the heat of adsorption with the van der Waals forces. It is not important whether these forces depend for the greater part on classical electrostatic dipole attraction or whether they arise, according to the newer concept of London,[236b] from wave mechanical resonance between vibrating quadrupoles. In any case it is illuminating that these forces excited even at molecular distances can only account for energies of the order of magnitude of the heats of vaporization. Those are quite small (a few kilocalories only; for example, a maximum of 11 kilocalories for sulphur dioxide on charcoal), as compared with the heats and activation energies of chemical reactions, which are up to one order of magnitude higher. It will, therefore, be anticipated that capillary condensation, in its broadest sense, is not the type of adsorption which brings about chemical activation of the substrate. Further, in most catalytic reactions, we are dealing with difficultly condensible gases at high temperatures, far above their critical temperatures, where capillary condensation, even when observable in the given system at lower temperatures, no longer occurs. Adsorption which is active chemically must, therefore, be of another type and its cause must be sought in other forces, and these the chemical forces.

Adsorption in Unimolecular Layers: It is obvious, without further discussion, that such forces can only be exerted on molecules associated directly with the adsorbent; quantum mechanical considerations indicate that the homopolar valence forces decrease exponentially with the distance. For the investigation of catalytically active adsorption it is necessary, therefore, to direct attention to the conditions prevailing in the first layer adsorbed, the unimolecular adsorbed layer.

[231] J. W. McBain, *Nature*, **117**, 550 (1926).

[232] A. Magnus, *Z. physik. Chem.*, A **142**, 401 (1929).

[233] M. Polanyi and K. Welke, *Z. physik. Chem.*, **132**, 371 (1928); F. Goldmann and M. Polanyi, *ibid.*, **132**, 321 (1928).

[234] E. Hückel, Adsorption and Capillarkondensation, Leipzig, 1928.

[235] H. Cassel, *Erg. exakt. Naturwiss*, **6**, 104 (1927).

[236] E. Jaquet, *Fortschr. d. Chem., Physik. u. physik. Chem.*, **18**, Heft 7 (1925).

[236a] J. W. McBain, Sorption of Gases and Vapours by Solids, Routledge, London, 1931.

[236b] London, *Z. physik. Chem.*, B **11**, 222 (1930).

Can the formation of this first adsorption layer in any way be observed? Naturally this is possible only if capillary condensation in the given system or under the given conditions of temperature and pressure does not occur at all. Under such conditions Langmuir [237] was able directly to calculate that, in his measurements at very small pressures, the minimal amounts of gas taken up by a solid surface sufficed to cover it unimolecularly. Paneth and Vorwerk [238] also found the same result in the adsorption of dyestuffs on minerals.

This type of adsorption apparently possesses a quite definite upper limit at that point at which the total surface is just covered with a unimolecular layer of adsorbate. The adsorption reaches, with increasing pressure (or concentration of solution), a saturation value. This is its important characteristic as contrasted with capillary condensation in the broad sense previously discussed. Since, now, the molecules of most of the simpler substances are approximately the same size (diameters of a few Ångström units), approximately equal numbers of all gases are adsorbed on a given surface; that is to say, it would be expected that the magnitude of the saturation value in moles on a given adsorbent is the same for all gases. This has been tested and found correct by Langmuir,[237] Rowe [239] and Benton.[240] It must be conceded that considerable deviations from this rule occur, but this can be understood if, for different gases, different fractions of the surface possess adequate binding energies.

In the cases just discussed, one observes the true adsorption, as we may term it, because, below the saturated vapor pressure or by reason of the adsorption forces [239, 241, 242, 243] at a somewhat lower pressure, capillary condensation is no longer possible. For the appearance of this true adsorption it is immaterial what the forces are which produce it; undoubtedly on every surface the unimolecular gas layer is to be found more or less saturated. It is remarkable, nevertheless, that the binding forces are very often sufficient to bind the " permanent " gases at high temperatures even to metals, as may be concluded from the kinetics of catalytic reactions. (See page 219 et seq.)

Multi-Molecular Layers: If, however, there occurs, by capillary condensation, further adsorption on this primary layer, as has been indicated

[237] I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
[238] F. Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445, 480 (1922).
[239] R. Rowe, *Phil. Mag.*, (7) **1**, 1042 (1926).
[240] A. F. Benton, *J. Am. Chem. Soc.*, **48**, 1850 (1926).
[241] W. C. Bray and H. D. Draper, *Proc. Nat. Acad. Sci.*, **12**, 295 (1926).
[242] S. Lenher, *J. Chem. Soc.*, 1785 (1926).
[243] G. Hoover and E. K. Rideal; *J. Am. Chem. Soc.*, **49**, 104, 116 (1927).

on page 182, there is nevertheless a possibility of observing occasionally the formation of the first layer. If it is formed by the aid of forces which are much stronger than the van der Waals forces, primary adsorption may already have reached saturation at pressures at which capillary condensation has not yet set in. This causes a marked second rise in the adsorption curve as shown in Fig. 24. The first horizontal portion of the curve indicates the attainment of saturation of the unimolecular layer. It may also happen [232] that the new rise sets in before saturation is reached, when, for example, repulsive forces in the adsorbate, or, according to Magnus,[244] dipoles orientated parallel to one another, delay the saturation.

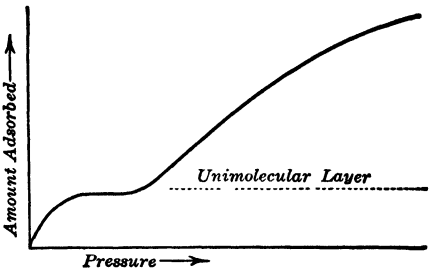


FIG. 24. Adsorption and Capillary Condensation.

Semenoff [245] has discussed theoretically the change from adsorption to condensation. He shows that it must set in suddenly in the manner shown in the diagram if studied above a certain definite pressure and below a certain limiting temperature. The phenomenon is manifested quite sharply in the condensation of supersaturated metal vapors from directed beams, concerning which a number of experiments, especially those of Estermann,[246] have been performed. We shall return to a more precise discussion of the deductions of Semenoff somewhat later (page 191).

In any case, the preceding considerations indicate that true adsorption, by directed forces, in a unimolecular layer, either alone or associated with the formation of an adsorbed "gas atmosphere," is actually observable. It is now necessary, owing to its importance in the phenomena of catalysis, to consider in detail the quantitative aspects of the subject. It was Langmuir [247] who theoretically derived these quantitative relations, confirmed them experimentally and utilized them in reaction kinetics.

The Adsorption Isotherm: Consider a gas, at pressure p, in dynamic equilibrium with a unit surface of which, under the given conditions, a fraction σ is covered with adsorbed molecules. The problem is to express this fraction as a function of the pressure, p, at constant temperature.

[244] A. Magnus, *Z. physik. Chem.*, A **142**, 401 (1929).
[245] N. Semenoff, *Z. physik. Chem.*, B **7**, 471 (1930).
[246] J. Estermann, *Z. Elektrochem.*, **31**, 441 (1925).
[247] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).

The law of the adsorption isotherm thus obtained is of especial importance because it permits an expression of the number of molecules in a position to react and thereby, also, in the majority of cases, a definition of the reaction velocity equation at constant temperature.

At equilibrium, according to definition, the number of molecules reaching and retained by the surface in unit time is equal to the number desorbed, that is, evaporated, in the same time. For the retention process, considering only the catalytically important case of pure unimolecular adsorption, only the bare surface $1-\sigma$ is significant. The number of molecules colliding with this surface is given by the Hertz-Knudsen formula [248]

$$N_0 (1 - \sigma) p \sqrt{\frac{1}{2\pi MRT}}$$

where N_0 is the Avogadro number and M the molecular weight. A certain fraction of these colliding molecules are retained by the surface. This fraction, which in the majority of cases differs but little from unity and is only slightly temperature sensitive, is known as the accommodation coefficient. The number of mols adsorbed per second will, therefore, be proportional to the pressure, and, therefore,

$$+\frac{d\sigma}{dt} = k_1 \cdot p(1 - \sigma).$$

The number of molecules leaving the surface in the same interval of time is dependent on the fraction of the adsorbate which, with the given statistical energy distribution, possesses the necessary energy. It is, therefore, proportional to the surface covered:

$$-\frac{d\sigma}{dt} = k_2\sigma.$$

Equating both velocities yields immediately the equilibrium condition:

$$\sigma = \frac{k_1 p}{k_2 + k_1 p}.$$

Introducing the adsorption coefficient $b = k_1/k_2$ there results

$$\sigma = \frac{bp}{1 + bp}$$

as the equation for the portion of the surface covered, or, multiplied by the appropriate magnitude, for the overall adsorbed amount expressed as surface.

[248] See K. F. Herzfeld, Kinetische Theorie der Warme, p. 29, Braunschweig, 1925.

The constant k_1 is, as can be seen from the equations above, only dependent on the square root of the temperature, is, therefore, itself only slightly temperature sensitive. On the other hand, k_2, which gives the fraction of the adsorbed molecules which possess more than the adsorption energy, λ (in calories per mol), must vary with temperature according to a Boltzmann exponential function:

$$k_2 = k_0 e^{-\lambda/RT}.$$

The adsorption coefficient, b, is, therefore, a quantity which decreases rapidly with increasing temperature

$$b = \frac{k_1}{k_0} \cdot e^{+\lambda/RT}.$$

This corresponds to the fact that adsorption is always less the higher the temperature. Since, in unimolecular adsorption, the heat of adsorption, λ, involves forces which, as has already been pointed out, are often of the nature of chemical binding energies, it follows that the steepness of the decrease in adsorption may be considerable (see page 193).

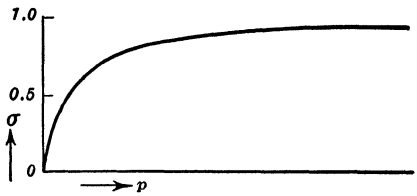


FIG. 25. Langmuir Adsorption Isotherm.

The variation of the adsorbed amount with the gas pressure is, on the basis of this adsorption isotherm, represented by a curve, shown schematically in Fig. 25 tending towards a limiting value of the adsorption with the surface completely covered.

Two special cases of this isotherm are of importance in reaction kinetics. For weak adsorption, or very low pressures, in general when $bp \ll 1$, there results

$$\lim \sigma_{p \to 0} = bp,$$

an equation which interprets the initial linear rise of the curve in Fig. 25. On the contrary, at high pressures, or with strong adsorption, in general when $bp \gg 1$, the surface layer will always be saturated, that is to say

$$\lim \sigma_{p \to \infty} = 1.$$

This portion of the isotherm is the nearly horizontal section of the curve indicating an asymptotic approach to saturation. Hence, it is only in the middle section of medium adsorption where the adsorption isotherm needs to be used in its complete form.

This kinetic derivation of the isotherm cannot carry the same conviction

as one derived from thermodynamics, just as the van't Hoff derivation of the mass action law is more illuminating than that of Guldberg and Waage from the velocities of the forward and backward reactions. The validity of the second law of thermodynamics possesses a higher degree of certainty than any molecular statistical assumption concerning velocities. It may, therefore, be noted as a great advance that Volmer [249] has been able to obtain the same equation by thermodynamic methods.

According to the second law of thermodynamics the work for the isothermal transfer of an infinitesimal amount of gas from the surrounding gas phase to the adsorption layer in equilibrium with it must be zero. This work is a combination of the work of compression of the gas and that of the expansion of the adsorbate

$$dA_{\text{gas}} - dA_{\text{ads}} = 0.$$

For the evaluation of these energy quantities in the given conditions of state, p and σ, of the equilibrium, it is necessary to have an extra-thermodynamic definition of the equation of state in gas and adsorbate, analogous to that of the ideal gas laws which must be introduced for the derivation of the law of mass action. For the gas we introduce the fundamental equation

$$pv = RT$$

For the adsorbate we make use of a very important observation of Volmer and Adhikari [250] according to which the binding to the adsorbent, even with binding forces chemical in nature,[251] is not of such a kind that the adsorbed molecules are held firmly to particular points on the surface. Rather, observation shows that a wandering of the adsorbed molecules over the adsorbing surface occurs. We can, therefore, look upon the adsorbed substance as a kind of gas in which free (or, at any rate, disordered) motion prevails, not in all directions of space but only in the two dimensions of the surface. To set up an equation of state for this " two-dimensional gas " we have to define its " pressure." Analogously to gas pressure, this pressure is the force operating on a unit of the boundary lines of the surface, which tends to expand the adsorbate and, therefore, to increase the surface. Such a force promotes a diminution of the opposed surface tension, γ. We can, therefore, use this diminution as a measure of the two-dimensional pressure

$$\phi = \gamma_0 - \gamma.$$

The equation of state of the two-dimensional gas has now to couple this

[249] M. Volmer, *Z. physik. Chem.*, **115**, 253 (1925).
[250] M. Volmer and G. Adhikari, *Z. physik. Chem.*, **119**, 46 (1926).
[251] G. Adhikari and I. Felman, *Z. physik. Chem.*, **131**, 347 (1928).

pressure, ϕ, with the surface per mol, Ω. That the ideal gas equation is not applicable in this case, is evident at once from the fact of a saturation adsorption. This signifies a finite and specific area, β, occupied by one mol of adsorbed molecules, which diminishes the free area of motion. Volmer, therefore, arrives at an equation for the adsorbate, analogous to that of van der Waals for non-ideal gases, of the form

$$\phi(\Omega - \beta) = RT.$$

Now, for the two energy quantities in question we have

$$v\,dp - \Omega\,d\phi = 0,$$

or

$$v\,dp = \Omega\,d\phi.$$

The two equations of state permit us to express p and ϕ in terms of v and Ω and we obtain

$$\frac{\Omega\,d\Omega}{(\Omega - \beta)^2} = \frac{dv}{v}.$$

With the simplifying assumption (which, it is freely admitted, limits the validity of the derivation) that $\beta \ll \Omega$, it follows that

$$\frac{d\Omega}{\Omega - 2\beta} = \frac{dv}{v},$$

or, integrating, and removing logarithms,

$$\frac{\Omega - 2\beta}{v} = \text{const} = k.$$

If we now introduce for the fraction of the surface covered,

$$\sigma = \frac{\beta}{\Omega},$$

and the gas pressure

$$p = \frac{RT}{v}$$

we obtain finally,

$$\sigma = \frac{\frac{\beta}{RTk}p}{1 + \frac{2\beta}{RTk}p},$$

that is, an equation quite analogous to that of Langmuir. The divergence consists in this, that, in this thermodynamic treatment, when $p = \infty$, in other words, at saturation, $\sigma = \frac{1}{2}$. This means that the molecules still have a portion of the surface area at their disposal for their own motion.

According to Schwab and Pietsch,[252] the derivation can be made somewhat more illuminating, but with the simplifying assumption introduced at a less acceptable point, by operating in the manner employed by van't Hoff in which the adsorption is conducted via an equilibrium box whose walls are in adsorption equilibrium with the gas content. The derivation given above is the original derivation of Volmer.

It may also be remarked here that Reichinstein,[253] at least simultaneously with Langmuir, derived the isotherm from quite other principles, using his " displacement-principle," that is to say, a kind of distribution law, coupled with the assumption that the sum of the mols adsorbed was constant.

Adsorption from Mixtures: The same form of the adsorption isotherm is thus obtained from very different modes of approach, so that, in future, we may use it as the basis of our kinetic considerations. For this purpose, a knowledge of adsorption from gas mixtures is of importance, since, even in the simplest reaction, at least two substances, reactant and product, are present, and, hence, must also be considered in adsorption. The conditions obtaining with gas mixtures are still quite uncertain, at least so far as the results of direct adsorption measurements are concerned; quite contradictory results have been obtained. Theory yields, on the contrary, for the idealized limiting case, a very simple assumption. Restricting the discussion to the kinetic approach to adsorption and designating the corresponding magnitudes of the second gas with the symbols p', b', σ', k', the condition of equilibrium is:

$$k_1 p(1 - \sigma - \sigma') = k_2\sigma,$$
$$k_1' p'(1 - \sigma - \sigma') = k_2'\sigma',$$

from which an adsorption isotherm, for each of the two gases, is obtained:

$$\sigma = \frac{bp}{1 + bp + b'p'},$$
$$\sigma' = \frac{b'p'}{1 + bp + b'p'}.$$

The presence of the second gas therefore diminishes the adsorption of the first proportionally to its partial pressure, p', and its adsorbability, b', which appear in the denominator. The gases mutually displace each other

[252] G.-M. Schwab and E. Pietsch, *Z. physik. Chem.*, B **1**, 385 (1929); *Z. Elektrochem.*, **35**, 573 (1929).

[253] D. Reichinstein, *Z. Elektrochem.*, **21**, 359 (1915); **31**, 593 (1925).

from the surface.[253] It further follows that:

$$\sigma : \sigma' = (p : p') \frac{b}{b'},$$

and hence, constancy of the adsorption relations at constant gas composition independent of the total pressure. Palmer [254] was able to confirm this conclusion. According to Cassel [255] thermodynamics only demands that:

$$\left(\frac{d \log p}{d\sigma'}\right)_{\sigma} = \left(\frac{d \log p}{d\sigma}\right)_{\sigma'}$$

a requirement which is actually fulfilled by the preceding expression.

The State of the Two-Dimensional Layer: The analogy between the two-dimensional gas in the adsorption layer and the free three-dimensional gas, which plays a rôle in the Volmer derivation, can be further extended. First, we can take into account, with many substances, the mutual attraction of the adsorbed molecules, in that, as van der Waals showed, we can introduce a corresponding pressure correction. It is known that, in this way, the van der Waals equation becomes a theory of condensation phenomena. In the present case, with certain substances adsorbed, we arrive at the formation of a two-dimensional liquid by increase of the adsorption density. As in liquid condensations, after attainment of the saturation pressure, there is no further increase of pressure so long as condensation is occurring; similarly, in the adsorbate, ϕ does not increase further until the whole surface is covered with a two-dimensional liquid. This is the change to capillary condensation, according to Semenoff,[245] which was mentioned previously, since, now, the three-dimensional liquid can readily form, the two-dimensional gas acting as the nucleus for its formation.

Also, an analogy to solid bodies may be imagined in the form of a "two-dimensional crystal." Below a certain temperature and especially with very strong binding forces, the adsorbed molecules may no longer be freely mobile but may be adsorbed more or less statically to the lattice points of the adsorbent, and hence in a regular structure.[256] The existence of such two-dimensional crystals has recently been demonstrable through the discovery of electron interference. The concept of motion of particles as wave processes has led to the conclusion that a beam of electrons is a wave packet of wave length

$$\lambda = \frac{h}{mv} = \sqrt{\frac{150}{V}} \cdot 10^{-8}$$

[254] W. G. Palmer, *Proc. Roy. Soc.*, A 110, 133 (1926).
[255] H. Cassel, *Physik. Z.*, 26, 862 (1925).
[256] A. Glaser, *Hand. d. Exp.-Physik.*, 8 Part 2, Leipzig (1929).

where λ is the wave length in cm., m is the mass of the electron, v the velocity of the electron, V the exciting potential in volts. It can be seen that electrons of exactly $150V$ possess a wave length of 1 Ångström unit, and that there is thus obtained waves of the same order of magnitude as those of Röntgen rays suitable for the investigation of crystals. The special characteristic of the new waves of matter is that, in consequence of their more powerful interaction with the crystal units, they are more strongly diffracted than Röntgen rays and that, therefore, their diffraction diagrams constitute a picture of the uppermost layers of the crystal. It could, therefore, be anticipated,[257] immediately after the discovery of the phenomenon, that they would be utilized in the investigation of crystal surfaces.

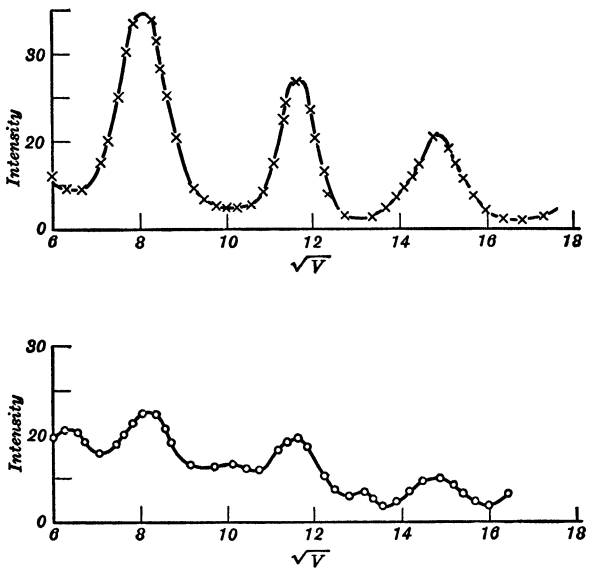


FIG. 26. Diagram of an Electron Beam from Nickel (upper curve) and from Nickel with Adsorbed Hydrogen (lower curve) (Rupp).

Germer [258] first took such pictures with nickel in the presence and absence of what was presumed to be hydrogen. On cooling heated nickel crystals at low gas pressures he obtained an intermediate interference diagram of a gas crystal, prior to the appearance of an amorphous layer, which latter was assumed to be multimolecular adsorption. In the intermediate state the individual hydrogen atoms were so arranged around the lattice

[257] G.-M. Schwab, *Erg. exakt. Naturwiss.*, **7**, 331 (1928).
[258] L. H. Germer, *Z. Physik.*, **54**, 408 (1929).

centers as to have twice the interatomic distances of the nickel atoms. Above 150° C. this diagram did not occur, that is to say, the melting point of the two-dimensional crystal was exceeded.

Rupp [259] reached the same conclusions. In Fig. 26, in the upper diagram, is shown the intensity versus $\sqrt{V}$ relations for the gas-free nickel crystal; underneath is shown the curve for the nickel with the adsorbed gas-crystal. It shows, as can readily be seen, maxima at the half distances, and, therefore, according to the Bragg relation, twice the lattice constant. Concerning Rupp's studies of a catalytic reaction by the method of electron interference more will be reported at a later stage (page 191).

At the high temperatures at which many catalytic reactions occur, especially with difficultly condensible gases, it can, however, certainly be assumed that both the melting point of the two-dimensional crystal and the critical temperature of the two-dimensional liquid will be exceeded and that the adsorption isotherm developed for a two-dimensional gas may be employed.

Deviations from the Adsorption Isotherm: It has been emphasized, latterly especially by Polanyi,[260] that the isotherm in most of the practical examples of adsorption measurements is not obeyed experimentally and that, in the cases where it holds, the temperature dependence of its constants (see page 187) is not fulfilled. This is regarded as a serious objection to the application of the Langmuir isotherm to the kinetics of catalytic reactions. The deviations, therefore, merit special discussion.

At the outset all those cases must be excluded in which the appearance of a saturation value has not been attained, and this constitutes the majority of all direct adsorption measurements. Such experiments can best be expressed by the empirical isotherm.

$$\text{Adsorbed Amount} = b_1 p^n$$

where n is a fraction. In such cases we may be dealing with adsorption in many layers, and, therefore, with processes which are not significant chemically.

Even, however, with unimolecular adsorption, deviations are often found, that is to say the constants of the Langmuir equation are not constant. Palmer [254] finds for example, with metals as adsorbents, that b/b', which, in the adsorption of mixtures, should be a constant, is, with hydrogen as one of the gases, always too large in favor of the hydrogen. On the other hand,

[259] E. Rupp, *Z. Elektrochem.*, **35**, 586 (1929).
[260] M. Polanyi, *Z. Elektrochem.*, **35**, 584 (1929).

Hurst and Rideal,[261] find, on the contrary, that, in the adsorption of hydrogen and carbon monoxide by platinum, the ratio increases with increasing total pressure in favor of the carbon monoxide. Such a behavior can be understood, as Hinshelwood has pointed out,[12] if the actual adsorbing surface can be regarded as the sum of many kinds of surface, with changing b ratios. In this case, with each gas, that part of the surface having the greater b value will first be covered and with a different progression of surfaces for each gas the observed phenomena are understandable. It is also to be expected that, on a somewhat rough surface, all the points do not have the same capacity for adsorption. The study of heats of adsorption will show that this assumption is directly confirmed.

Is not then the introduction of constant b-values into the kinetics of catalysis unjustified? The conclusions concerning adsorption that can be reached from velocity determinations, practically always show that the *fraction* of the adsorbing surface on which the catalysis occurs (it is for the most part a quite small fraction) possesses a constant b. It is only on the most active portions of the surface that the velocity assumes observable magnitudes. Those areas which adsorb to measurable extents and with varying b, are, in their chemical effects, subordinate and are the areas on which catalysis is slow. We shall have occasion frequently to return, in more detail, to these facts which have extraordinarily developed our conception of catalytic phenomena. At this stage it is sufficient to conclude that the derived isotherms do not need to be strictly applicable to the measured adsorptions in order accurately to describe the catalytically active area of adsorption. (Schwab.[262])

Heats of Adsorption

Indirect Methods of Measurement: The heat of adsorption, as has already been pointed out on page 187, is given by the steepness of the temperature decrease of the adsorption constant, b, according to the equations,

$$b = \frac{k_1}{k_0} \cdot e^{\lambda/RT} \quad \text{or} \quad \frac{d\,ln\,b}{d(1/T)} = \frac{\lambda}{R}.$$

In this manner, by a suitable evaluation of the adsorption measurements at different temperatures, λ may be determined.

This is true, however, only as long as b is actually a constant at each temperature, independent of the pressure or the fraction, σ, of the surface covered. We have just seen that this condition is seldom fulfilled in actual

[261] W. Hurst and E. K. Rideal, *J. Chem. Soc.*, **125**, 694 (1924).
[262] G.-M. Schwab, *Z. Electrochem.*, **35**, 585 (1929).

adsorption measurements and that, rather, with increased covering, progressively less adsorbent portions of the surface, with falling values of b, become involved. For this reason, neither constant nor correct values of the heat of adsorption are obtained.

A better method, therefore, is a comparison of the equilibrium pressures at constant fraction of surface covered and different temperatures. For such equilibrium pressures, as for the pressures of an evaporating liquid, the Clapeyron-Clausius equation holds,

$$\frac{d\ ln\ p}{d(1/T)} = -\frac{\lambda}{R}.$$

Differential and Integral Heats of Adsorption: By applying this method there is obtained, directly, the heat of adsorption corresponding to the given amount of adsorption, and, hence, the heat which would be yielded if, at the given saturation, one mol of gas were adsorbed in addition to an infinitely large amount already adsorbed. This is the differential heat of adsorption. It is to be distinguished from the integral heat of adsorption which is the average heat of adsorption per mol for all the gas adsorbed by an originally clean surface up to the adsorption in question. If the differential heat of adsorption was constant, that is to say, if the first gas adsorbed gave the same heat effects as the succeeding gas, the differential and integral heats would be identical. In practice, however, a distinction between the two is nearly always necessary.

Direct Methods of Measurement: In addition to such methods, there is also the direct method of measurement of the heats of adsorption with a calorimeter. In this case the integral heat of adsorption may be measured by introducing to the evacuated adsorbent a single large volume of gas, measuring the adsorbed amount by pressure measurements and the resulting heat effect with the calorimeter. One can, however, equally well measure the integral heat of adsorption over a very small interval of the adsorption region by adsorbing small amounts of gas stepwise. This has been the most usual procedure, at least for the discussion of the problem. In this manner, values are obtained which are to be regarded as very near to the differential heats of adsorption for the mean area covered.

A vacuum calorimeter for such purposes employed by Taylor, Kistiakowsky and Flosdorf [263] is shown in Fig. 27 having an external heating unit for calibration and in the interior a platinum resistance thermometer with a sensitivity of one ten thousandth of a degree. The special feature

[263] H. S. Taylor, G. B. Kistiakowsky and E. W. Flosdorf, *J. Am. Chem. Soc.*, **49**, 2200 (1927).

of its construction should be noted consisting as it does of a resistance thermometer, which carries the electrical current, practically completely surrounded by the adsorbent. So far as its stationary temperature is concerned, the thermometer is dependent on the thermal conductivity of this adsorbent. As we shall see later (p. 200) this factor carries with it certain unexpected disadvantages.

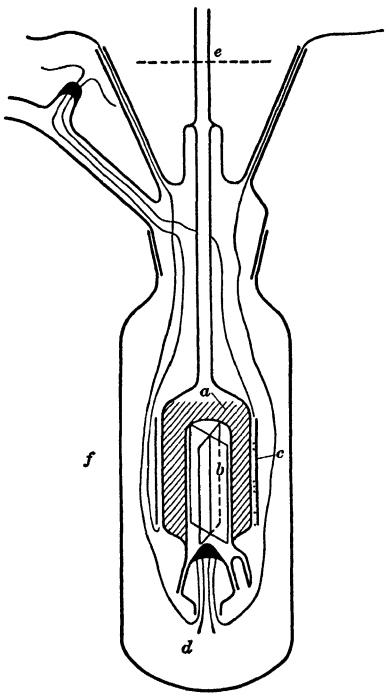


FIG. 27. Adsorption Calorimeter (H. S. Taylor, Kistiakowsky and Flosdorf). (*a*) Adsorbent, (*b*) Platinum Resistance Thermometer, (*c*) Heating Coil, (*d*) Vacuum Jacket, (*e*) Gas Inlet, (*f*) Ice Thermostat.

Magnus and Giebenhain [264] employ another construction which is equally serviceable but, because it employs compensation thermocouples, and divides the adsorbent volume by metal discs, it avoids the disadvantages of the previous construction.

The data deduced from the Clapeyron-Clausius equation agree well, in general, with the calorimetrically determined differential heats of adsorption so that they merit a degree of trust.[264, 265] All the measurements thus performed have actually confirmed the conclusion that we reached in the preceding section concerning the cause for the inapplicability of the Langmuir isotherm, namely, that the surface possesses areas of unequal energies. This is shown, in the calorimetric work, in that the first quantities of gas that are taken up by the clean surface practically always develop larger quantities of heat than later quantities of gas taken up by the partially covered surface. This result definitely indicates that different positions on the surface possess different capacities for adsorption and one can, therefore, understand that they show varying b values. One cannot, of course, assume that at first only the positions with the greatest heats of adsorption are saturated and the others not at all, then the next smaller in heat value and so on; but by intelligent superposition of successive adsorptions with varying intensities at different areas of the surface, the

[264] A. Magnus and H. Giebenhain, *Z. physik. Chem.*, A **143**, 265 (1929).
[265] A. Magnus and R. Kieffer, *Z. anorg. allgem. Chem.*, **179**, 215 (1929).

expected curve can be readily obtained,[266] which shows, as do the measurements, a decrease of the heat of adsorption with increasing area covered. The heat of adsorption of hydrogen on copper which has been slightly poisoned is shown in Fig. 28. It may be stated, without giving further examples, that practically all measured differential heats of adsorption show such a more or less marked decrease with increased coverage.

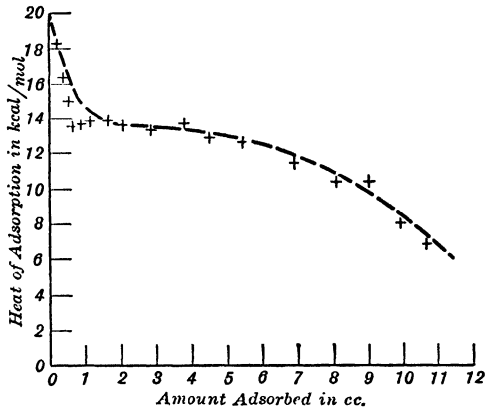


FIG. 28. Heats of Adsorption of Hydrogen on Poisoned Copper (Taylor).

Anomalous Results: Before drawing our conclusions from these facts we must discuss some anomalies which have been obtained in such investigations. These concern the absolute value of b in its dependence, on the one hand, on the heat of adsorption and, on the other, on the surface covered. We defined b above as the ratio of the kinetic constants, k_1/k_2. It can, however, also be defined thermodynamically as an equilibrium constant. In the region of small, linear adsorption ($\sigma = bp$) we can set up the relation

$$\frac{N_{ads}}{N_{gas}} = \frac{\sigma \cdot O \cdot RT}{\beta \cdot p} = \frac{O \cdot RT}{\beta} b$$

where O designates the total available surface per cubic centimeter of gas expressed in cubic centimeters volume of the unimolecular layer (see page 240); N is the number of molecules in each of the two states. On the other hand, according to the Boltzmann relation, we have

$$\frac{N_{ads}}{N_{gas}} = O \cdot v \cdot e^{\lambda/RT}$$

where v is the *a priori* probability that a molecule is to be found in the adsorbed condition. (The "*a priori*" signifies that the probability is without reference to the energy relations which are contained in the exponential term; this factor corresponds to the number of possibilities of realizing the given state.) We thus derive from the two expressions that

$$b = \frac{\beta v}{RT} e^{\lambda/RT}.$$

[266] H. S. Taylor and G. B. Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927).

It would, therefore, be expected, at any rate in the linear region of adsorption where b is undoubtedly constant, that owing to the simple relation between the two, λ, the differential heat of adsorption should be independent of the surface covered. This is not the case in studies made thus far. Kälberer, Mark and Schuster [267] found that, with both bauxite and silica gel, with different gases, the heat of adsorption is variable even in the range of linear adsorption and, indeed, increasing with increasing coverage so that centers with higher heats of adsorption came after those with lesser heats. Further, they found that, by varying the adsorbent, the adsorption for a given gas, and, with different gases, the adsorption on a given adsorbent, did not vary according to the above equation but that βv is dependent on the heat of adsorption. This interdependence so operated that an increase of λ is compensated in its influence on b by a diminution of βv, approximately according to the relation

$$\beta v = e^{-\lambda/RT} \text{ const.}$$

Formally, this interprets the constancy of b in spite of the increasing heats of adsorption.

It is difficult qualitatively to understand this variation of βv, and still more difficult to derive it quantitatively. Either it must be assumed that, with increasing heats of adsorption, the motion of the adsorbed molecules decreases [232] and, with this, the value of β, which comprises the assumed adsorption volume; or, it may be assumed, as was done quantitatively by Dunkel and Mark [267] and qualitatively by Schwab and Pietsch [252] that v, the *a priori* probability, is not constant, but that positions on the surface first come into operation which have relatively small heats of adsorption but large possibilities of adsorption. These positions may be located in the boundary lines of " pools " or " islands " of adsorbate. Later, with increased coverage, the adsorbate can transfer from these positions to those of higher adsorption energy but smaller *a priori* probability, to the active centers of the adsorbent, thus producing the rise in the heat of adsorption. Thermodynamically this means that, with an increase in the energy, an increase in the entropy is coupled. We shall return to this possibility immediately.

Anomalous Initial Heats of Adsorption: Still more remarkable are the results which different investigators have obtained for the very first heats

[267] H. Kälberer and H. Mark, *Z. physik. Chem.*, **139**, 151 (1928);
H. Kälberer and C. Schuster, *ibid.*, **141**, 270 (1929);
M. Dunkel and H. Mark, *Monatsh.*, **53-54**, 764 (1929);
H. Kälberer, H. Mark and C. Schuster, *Z. Elektrochem.*, **35**, 600 (1929).

of adsorption of gases on highly active catalysts,[263, 268, 269] and even on active charcoal.[270] Under certain circumstances, especially with calorimeters of the type shown in Fig. 27, the differential heats of adsorption appear to pass through a maximum which lies at very low amounts of adsorption. Fig. 29 shows such a case, the heat of adsorption of hydrogen on pure copper as a function of the surface covered.

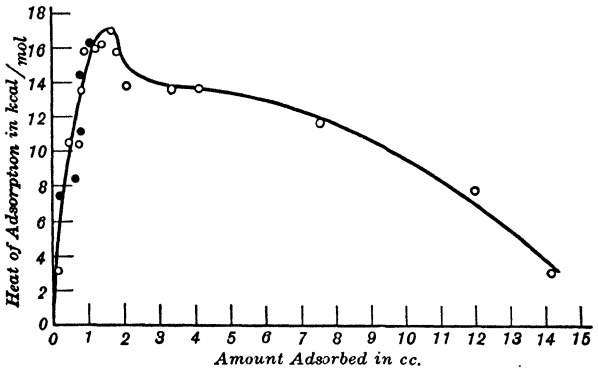


FIG. 29. The Maximum in the Heats of Adsorption of Hydrogen on Copper (Taylor).

The falling branch of the curve is readily explained by the decreasing adsorption capacity of the surface; here the value of b simultaneously decreases, for these areas adsorb at higher pressures than the first. In the rising section of the curve, b, however, is not only inconstant, but, in contrast to the results obtained by Mark, it decreases with increasing heat of adsorption. The centers which yield the maximum adsorb later than the first with their smaller heats of adsorption.

The difficulties of interpreting such a result are greater to a much higher degree. From the change of the position of the maximum with pretreatment of the adsorbent Taylor and his co-workers[266] concluded that the small first heats of adsorption were on the chemically active points. On these, the heats of adsorption were still higher than those at the maximum but were thermometrically not measurable because they were partially consumed in an activation process on the substrate. Later measurements did not show such simple relations.[271] Also, as the authors themselves ad-

[268] C. F. Fryling, *J. Phys. Chem.*, **30**, 818 (1927).
[269] B. Foresti, *Gazz. Chim. Ital.*, **54**, 132 (1924); **55**, 185 (1925).
[270] W. E. Garner, *Trans. Farad. Soc.*, **22**, 71 (1926), *Nature*, **124**, 409 (1929).
[271] E. W. Flosdorf and G. B. Kistiakowsky, *J. Phys. Chem.*, **34**, 1907 (1930).

mitted,[263] this concept involved a thermodynamic difficulty, which they invited Herzfeld to examine.

Herzfeld [272] attempted to interpret the rising branch of the curve by the assumption of a changing *a priori* probability, v. It may here be remarked that this changing v is to be associated with a change of the chemical constants, and, partially, of the specific heat terms in the equation of the reaction isochore. For, if one expresses b logarithmically there results

$$\log b = \frac{\lambda}{RT} + \log \beta v - \log RT,$$

whence it follows that $\log \beta v$ contains the terms of the isochore just mentioned. Herzfeld studied, therefore, whether v could be decreased on the most active centers because the adsorbed molecules on these positions were limited in their degree of freedom (of motion or probability of a given energy state) to a greater degree than on other areas of the surface, for example, through differences of vibrational frequencies towards the adsorbent or, within the molecule, loss of rotational degrees of freedom. It was shown that these effects, at the most, could only account for a few kilocalories in the heats of adsorption, that is, it would explain maxima of the height of a few kilocalories.

The only possibility of interpreting a maximum of the height in question would appear to be in the principle already discussed by Mark and Dunkel.[267] According to these authors the rise in the heat of adsorption would depend upon an increasing formation of molecule-pairs due to van der Waals forces of attraction. The form of the rise (Fig. 29) cannot be reproduced, however, on this assumption.

As a result of this very unsatisfactory theoretical situation the experimental bases of the problem have been carefully re-examined. As a result, Schwab and Brennecke [272a] found that the effect was dependent upon a peculiar behavior of the system, gas-adsorbent, by reason of its thermal conductivity. A metal powder is a poor conductor of heat, so that the heat conductivity must be taken care of for the most part by the gas present. The heat transfer from a gas to a solid surface is very dependent on the pressure. On admission of gas to the adsorbent, or on evacuation, the heat of adsorption is falsified because the stationary temperature of the thermometer (Fig. 27), at which the measurement is made, changes, an effect which is particularly manifest at low pressures and therefore at small adsorptions. If this effect be measured and corrections applied, the heat of

[272] K. F. Herzfeld, *J. Am. Chem. Soc.*, **51**, 2608 (1929).

[272a] G.-M. Schwab and Brennecke, *Z. physik. Chem.*, Bodenstein Festband 907 (1931); B **16**, 19 (1932).

adsorption is found to fall steadily, just as in those calorimeters which measure integral heats, such as the ice calorimeter, and in the calorimeters such as those of Magnus and Giebenhain which are strictly isothermal. In recent years, Beebe and his co-workers have elaborated the measurements of heats of adsorption on catalysts with great refinements of technique with measurements extending to very small adsorptions.[272b]

Hence the anomaly of the first heats of adsorption can be discounted and we may now examine what the measurements of heats of adsorption can teach concerning heterogeneous catalysis.

TABLE XXIX—HEATS OF ADSORPTION ON CATALYSTS

Gas	Adsorbent	in Kilocals.	Observers
H_2	Cu	9.6	Beebe and Taylor [273]
H_2	Cu	20	Taylor and Kistiakowsky [266]
H_2	Cu	11.3	Washburne [274]
H_2 and D_2	Cu	11	Beebe et al. [272b]
CO	Cu	20–13	Beebe [272b]
CO	Cu	10	Taylor and Kistiakowsky [266]
NH_3	Cu	7	Dew and Taylor [276]
C_2H_4	Cu	16	Washburne [274]
C_2H_6	Cu	11	Washburne [274]
C_2H_5OH	Cu	14	Hoover and Rideal [243]
H_2	Ni	20.6	Beebe and Taylor [273]
H_2	Ni	15	Dew and Taylor [276]
NH_3	Ni	11.3	Dew and Taylor [276]
NH_3	Fe	16	Dew and Taylor [276]
NH_3	Fe	18	Taylor [274]
H_2	Pt	30–10	G. B. Taylor, Kistiakowsky and Perry [276a]
O_2	Pt	80–20	G. B. Taylor, Kistiakowsky and Perry [276a]
O_2	C	70–115 (High temperature)	Garner and McKie [277]
O_2	C	20–40 (Low temperature)	Ward and Rideal [278]

[272b] Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932); *J. Phys. Chem.*, **30**, 1538 (1926); Beebe and Wildner, *J. Am. Chem. Soc.*, **56**, 642 (1934); Beebe et al., *ibid.*, **57**, 2527 (1935); **58**, 1703, 2196, 2661 (1936).

[273] R. A. Beebe and H. S. Taylor, *J. Am. Chem. Soc.*, **46**, 43 (1924).

[274] H. S. Taylor, *Z. Elektrochem.*, **35**, 545 (1929).

[275] R. A. Beebe, *J. Phys. Chem.*, **30**, 1538 (1926).

[276] W. A. Dew and H. S. Taylor, *ibid.*, **31**, 277 (1927).

[276a] G. B. Taylor, G. B. Kistiakowsky and J. H. Perry, *J. Phys. Chem.*, **34**, 799 (1930).

[277] W. E. Garner and D. McKie, *J. Chem. Soc.*, 2451 (1927).

[278] A. Ward and E. K. Rideal, *ibid.*, 3117 (1927).

Magnitude of Heats of Adsorption on Catalysts: First of all, the magnitudes of the heats of adsorption are of importance. Excluding the cases of pure dipole adsorption, in which heat effects little in excess of heats of evaporation have been obtained (see page 183), it may be observed that, for adsorptions of gases on catalytically active adsorbents, values of the order of magnitude of chemical heats of reaction are obtained. In the preceding table some of these values are collected.

Nature of Catalytic Adsorption: From the size of these values it can be deduced that the adsorption in these cases is, in its nature, that of a true chemical binding; for example, the binding of carbon monoxide to copper should be of the same nature as that of carbon monoxide in nickel carbonyl that is to say, a homopolar bond which results from the specific interaction energies of the participating atomic systems, wave-mechanically expressed as resonance. We shall see later that precisely this identification of catalytically active adsorption with the true chemical bond has proved itself to be extraordinarily fruitful for the interpretation energetically of reaction acceleration.

The difference between such an adsorption and a chemical bond is in reality one of convention. If the bound atoms can detach themselves from the lattice of a metal, for example, and can form a complete molecule such as nickel carbonyl, $Ni(CO)_4$, we are accustomed to speak of compounds, because, in such cases, the law of constant proportions is applicable. If, however, the metal atom (Cu) still remains partially bound to the metal lattice (the considerations in question applying naturally to other lattices with other components) there is no question of a stoichiometric determination of the combining ratio since this depends upon the surface development of the adsorbent. We now speak of adsorption (concerning Chemosorption, see page 179). One might, however, equally well speak of a surface compound. The question, whether the interpretation of heterogeneous catalysis by means of adsorption or by the use of intermediate compounds is to be preferred, is without meaning from this standpoint, since both mean essentially the same thing as far as chemical adsorption is concerned. Also, the heuristic value of the concept of intermediate compounds which Neumann [279] sees as its greatest advantage, is not impossible to the adsorption concept in the form indicated, since the question whether a given surface compound is to be expected still remains a question of " chemical instinct." It is only that the chemical possibilities are increased by a number of compounds which cannot be isolated away from the surface. The fact that a substance may be isolated is, however, according to Ostwald

[279] B. Neumann, *Z. Elektrochem.*, **35**, 42 (1929).

(see page 71), no argument for or against the catalytic rôle of an intermediate compound.

Significance of Variable Heats of Adsorption: The second important conclusion from the experimental results is that the heats of adsorption on active catalysts practically always decrease with increasing adsorption. This can be regarded as a confirmation of the conclusion already reached from experience with the adsorption isotherms, namely, that the surface consists of energetically different areas with progressively decreasing heats of adsorption. Precisely this variability of heats of adsorption provided Taylor with direct experimental support for his theory of "active centers" [280, 281] of the catalytic surface* (see pages 280 et seq.), a theory which he originally deduced mainly from purely catalytic-chemical and kinetic results. These arguments, which alone are quite compelling, will be detailed later.

Qualitatively, then, we can record the fact of the energy differences of the surface as the second conclusion from the measurements of heats of adsorption. Quantitatively, from such measurements, we should be able to work out completely the energetic structure of the surface (an example

[280] H. S. Taylor, *J. Phys. Chem.*, **30**, 145 (1926).

[281] H. S. Taylor, *Proc. Roy. Soc.*, A **108**, 105 (1925).

* Sauter [229] has attempted to reverse this theory. The argument is as follows: On a charcoal on which the first adsorption of carbon dioxide deviated from the normal adsorption equilibrium of charcoal and had yielded falling heats of adsorption from an initial heat in the neighborhood of 20–30 kilocals., Magnus, Sauter and Kratz [282] were able, by thorough purification of the material, to obtain a linear start to the adsorption isotherm and to decrease the first heat of adsorption to 7.5 kilocals. . . The deviations in the adsorption isotherm, and the heats, obtained with the unpurified material, are therefore to be ascribed to the presence of traces of alkalis or alkaline earth oxides in the charcoal whose energetic and highly exothermic conversion to carbonates was measured as the first heats of adsorption. From this experiment Sauter concludes that the decrease in the heats of adsorption with increased catalyst surface covered may likewise be only illusory, and that the kinetic demonstration of active centers may not rely to any degree on the energetic evidence.

The objection to this generalization naturally lies in the assumption that the impurities in a charcoal and the homogeneity of its surface after purification are proof that for every other adsorbent and every catalyst the presence of high heats of adsorption is to be ascribed to obscuring impurities. According to such a theory, the greater velocity of reaction on the active areas should not lie in the energy of these latter but in the greater lifetime of the adsorbate on them. This means, however, nothing else than a larger b, and yet Herzfeld has already shown that the variations in b with the same surface energies can only be very small. Apart from these considerations, the assumption of a completely active surface is today no longer reconcilable with a whole series of experimental facts, as will be made clear in detail later.

[282] A. Magnus, E. Sauter and H. Kratz, *Z. anorg. allgem. Chem.*, **174**, 142 (1928).

of this can be seen; Taylor, *Z. Elektrochem.*, **35**, 545 (1929) and page 282); furthermore, we should be able directly to measure the first heats of adsorption of the reactants, which, from the energetic requirements of the reaction, go to the active centers. Unfortunately, this possibility, which would be extraordinarily important, is more one of principle than practice, for the following reasons. In some cases, the fall of the first heats of adsorption is so steep that extrapolation is too uncertain; in other cases, the initial anomalies already discussed intrude and, finally, the temperatures at which one measures adsorptions are generally quite different from those at which the catalytic reactions occur (see Taylor [274]). So long as these difficulties exist, the results of adsorption measurements obtained on the gross surface are only transferable with caution to the catalytically active fraction. The results of experiments which refer directly to the active areas, in other words, kinetic measurements, are, at the present time, more fruitful for the characterization of the catalytic surface. It is not proper to reject such conclusions, as would Sauter,[229] because, as yet, there do not exist any analogous calorimetric data.

Activated Adsorption

The existence of two separate and distinct types of adsorption, indicated so frequently in the preceding pages, has recently been more definitely established by reason of investigations in which it has been shown that, on a single adsorbent, a given gas may, under one set of conditions, be adsorbed practically exclusively in the one form and under other conditions practically exclusively in the other form. The definition of the conditions under which each type of adsorption may occur brings out quite intelligently the connection between processes of catalytic change and that form of adsorption which we have hitherto discussed as unimolecular adsorption or chemical adsorption. The newer work also has exhibited hitherto unappreciated characteristics of the latter type of adsorption.

Dual Adsorption on a Single Surface: In the older literature of adsorption there is a certain amount of sporadic evidence that adsorptions of two types may occur with a given gas on a single surface. Dewar [282a] showed that the adsorption of oxygen on charcoal at liquid air temperatures involved a heat of binding of 3750 calories per mol and that the oxygen was readily recoverable by pumping. At 0° C. Keyes and Marshall [282b] found a heat of adsorption of 72,000 calories for the first gas adsorbed and a

[282a] J. Dewar, *Proc. Roy. Soc.*, A **74**, 126 (1904); *Proc. Roy. Inst.*, **18**, 184 (1905).
[282b] Keyes and Marshall, *J. Am. Chem. Soc.*, **49**, 156 (1927).

difficult recovery mainly as oxides of carbon. Langmuir [282c] found that carbon monoxide was adsorbed by platinum and readily recovered at liquid air temperatures but was relatively irreversibly adsorbed at room temperatures and higher. Langmuir also found that the amount of oxygen adsorbed at liquid air temperatures by platinum was only one tenth of that at room temperatures under the same pressure conditions and that adsorbed in the higher temperature range is only removable by reaction with other gases. Nikitin [282d] came to a similar conclusion with respect to the adsorption of hydrogen by finely divided iron and nickel. He believed that the liquid air temperature adsorption was true adsorption; that at room temperatures and upwards was greater than at liquid air in the case of nickel and suggested to him a nickel-hydrogen compound at the surface. With iron the high temperature sorption of hydrogen was ascribed to solution.

Benton and White [282e] decisively demonstrated the two types of adsorption of hydrogen on finely divided nickel in that they extended the measurements of adsorption of hydrogen from the range studied by Gauger and Taylor,[282f] 0° – 300° C., to temperatures as low as −195° C. The newer data exhibit a minimum around −190° C. and between this temperature and −110° C. there is approximately a four-fold increase in adsorption. Above this temperature range, at various pressures, there is again a decreasing, but reversible, adsorption with increase of temperature. Benton and White concluded that "at the lowest temperatures the adsorption was of the secondary ' or ordinary molecular type, while at higher temperatures a progressively larger fraction of the nickel surface is capable of holding the hydrogen by adsorption of the ' primary ' type, involving a marked activation of the gas."

The Concept of Activated Adsorption: It was next pointed out by Taylor [282g] that the non-occurrence of the stronger type of binding of a gas to a surface at the lower temperatures could be satisfactorily explained if it were assumed (*a*) that the molecular or van der Waals type of binding was rapid, condensation probably occurring from a large fraction of collisions with the adsorbing surface and (*b*) that the specific adsorption in the higher temperature range involved higher heats of adsorption and was a relatively slow process requiring an activation energy for its achievement,

[282c] I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
[282d] N. Nikitin, *Z. anorg. allgem. Chem.*, **154**, 130 (1926).
[282e] A. F. Benton and T. A. White, *J. Am. Chem. Soc.*, **52**, 2325 (1930).
[282f] A. W. Gauger and H. S. Taylor, *J. Am. Chem. Soc.*, **45**, 920 (1923).
[282g] H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 578 (1931).

by reason of which activation energy, the term " activated adsorption " was employed. With these assumptions the observed increases of adsorption with increase in temperature would necessarily follow. The extent to which the two types of adsorption could be separated one from the other in the experimental measurements would depend upon the relative values of the two heats of adsorption and also on the magnitude of the activation energy of the high temperature process. A decisive test of such a point of view was immediately practicable, as the evidence available in the catalytic literature concerning oxide catalysts which function in a hydrogenating capacity indicated that the activation energy for the high temperature adsorption of hydrogen on such oxide surfaces should be materially higher than that obtaining with metals, since, catalytically, such oxides operate, in general, in a higher temperature range than do the hydrogenating metals.

Such a test, carried out by Taylor and Williamson,[282h] abundantly verified this point of view in the case of a mixed manganese-chromium oxide catalyst such as might be used in the hydrogenation of carbon monoxide to yield methanol. The minimum in the adsorption isobar was shifted in this case from the liquid air temperatures obtaining with metals (Benton and White) to temperatures in the neighborhood of 0° C. At −78° C. the adsorption of hydrogen was small, rapidly attained, and mostly reversible by evacuation at the same temperature; an adsorption of the van der Waals type. At 0° C., the adsorption of this type is smaller but there sets in an extremely slow adsorption, the rate of which makes perceptible changes in adsorption measurable only over periods of hours and days. At 100° and 132° C. where the van der Waals adsorption has fallen to negligible proportions the rate of this activated adsorption has now risen to conveniently measurable velocities, and, from such measurements, activation energies of adsorption could be calculated. The velocity of the adsorption increases rapidly with temperatures but the amount of adsorbed hydrogen at 184 and 305° C. rises to fifteen-fold that obtaining under similar pressures at −78° C. At 444° C. the extent of adsorption is still several fold that at −78° C. but definitely less than at 305° C. The increased adsorption is a real adsorption phenomenon, obeying the equation for the adsorption isotherm, and completely reversible, all of the hydrogen being recoverable by evacuation.

The Activation Energy and Heat of Activated Adsorption: There are two methods available by which activated adsorption may be characterized, the one involving a determination of the velocity of such adsorption, the

[282h] H. S. Taylor and A. T. Williamson, *J. Am. Chem. Soc.*, **53**, 813 (1931).

other a measurement of the heat of activated adsorption either calorimetrically or by deduction from isotherms of activated adsorption. With some systems both methods have been applied. It can be shown that, in certain circumstances, only one or the other is available, and in still other circumstances the methods can only be employed qualitatively but not quantitatively.

With manganese oxide-chromium oxide, Taylor and Williamson [282b] applied both criteria to the adsorption of hydrogen. From the velocity data at 100° and 132° C. the activation energy E of the adsorption process was calculated by means of the equation,

$$\log v_1 - \log v_2 = \frac{E}{4.58}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

in which, for the velocities v_1 and v_2 at temperatures T_1 and T_2, use was made of the times required for the activated adsorption of equal volumes of gas on a clean surface. In this way it was found that, on the first areas of the surface covered (10 ccs. adsorbed), the velocity was relatively rapid and the activation energy small (E = 5200 calories per mol). With increasing surface covered the velocity of adsorption sinks, whereas the activation energy rises consistently. The activation energy for the 10th to the 15th cc. adsorbed averaged 9500 calories per mol and, for the 15–25 cc. range, 10,400 calories. These data add another factor to those important in the heterogeneity of reaction surfaces subsequently to be discussed in detail under the theory of active centers (p. 280). It is evident that, on the most active areas, the velocity of activated adsorption is very much more rapid than on the less active areas of the surface. Thus, for example, on two areas of the surface at present under discussion having, let us assume, activation energies of 3000 and 5000 calories respectively, areas covered in the adsorption of the first 10 ccs., the velocities of adsorption at a temperature of 127° C. = 400° K. are in the ratio $e^{-3000/RT} : e^{-5000/RT} = e^{+2000/RT} : 1 = e^{2.5} : 1 = 12.18 : 1$. The velocity is twelve-fold more rapid on the former than on the latter. We shall see that this is a factor of fundamental importance in the problem of promoter action (p. 310).

The magnitude of the activation energy indicates also the reason for the absence of the activated type of adsorption at the lowest temperatures. Thus, employing an activation energy of 6000 calories for the first 10 cc. of activated adsorption, the ratio of velocities at 127° C., 27° C., and −73° C. is given by the expression $e^{-6000/800} : e^{-6000/600} : e^{-6000/400} = e^{-7.5} : e^{-10} : e^{-15} = e^{7.5} : e^{5} : 1 = 1801 : 148.4 : 1$. The velocity is twelve-fold greater at 127° than at 27° C. and the velocity is 150-fold less at −73° than at room temperature. Calculation shows that it would have required times

of the order of 120 hours for 10 cc. of activated adsorption to have occurred at −78° C. on a surface having a uniform activation energy of 6000 calories per mol.

Taylor and Williamson also deduced the heat of activated adsorption of hydrogen on manganese oxide-chromium oxide from the well known equation connecting heat of adsorption, pressure and temperature,

$$\log p_1 - \log p_2 = \frac{\lambda}{4.58}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where λ is the heat of adsorption, p_1 and p_2 are the equilibrium pressures for a given adsorption at T_1 and T_2 respectively. Using this equation, the data from the adsorption isotherms at 305° and 440° C., at which temperatures equilibrium data were obtained, indicate a heat of activated adsorption greater than 19,000 calories per mol whereas the heat of van der Waals adsorption calculated from similar data in the region of −78° to 0° C. show a heat of adsorption of approximately 1900 calories. The distinction between the calorimetric effects is manifest. The magnitude of the divergence serves also to account for the very pronounced increase in the amount adsorbed at the higher temperatures.

Thus far, the cases in which both criteria have been employed for a given gas-adsorbent system are few and are confined principally to systems involving hydrogen gas and oxide surfaces. A variety of reasons are responsible. In the case of metal hydrogen systems, the activation energies are small and the difficulties of velocity measurements in the region between −190° and −110° C., which would be the temperature range to be studied, are very pronounced. Nevertheless, in these cases, the heats of adsorption are capable of establishing the difference between the two types. At low temperatures (circa 90° K.) the heats of adsorption of hydrogen on copper and nickel are of the order of 1000 calories per mol. At room temperatures the heats of activated adsorption are in the range, 10,000 to 15,000 calories. In carbon monoxide-adsorbent systems the temperature ranges of van der Waals and activated adsorptions overlap, so that it is not possible to separate the two occurrences cleanly one from the other. Nevertheless, convincing evidence of activated adsorption of carbon monoxide on palladium has been obtained by Taylor and McKinney [282j] and by Williamson [282k] in the carbon monoxide-manganese, chromium oxide system.

The Data of Activated Adsorption: Owing to the comparative newness of the work concerning this problem of activated adsorption the experi-

[282j] H. S. Taylor and P. V. McKinney, *J. Am. Chem. Soc.*, **53**, 3604 (1931).
[282k] A. T. Williamson, *ibid.*, **54**, 3159 (1932).

mental material is widely scattered through the recent literature and has not hitherto been assembled. It may be, therefore, desirable to collect the principal results achieved in this field up to the present time. Much of this work is summarized in the following table which shows the adsorptions meas-

TABLE XXX — DATA ON ACTIVATED ADSORPTION

HYDROGEN

Adsorbent	$P_{mm.}$	Adsorption in cc. per 100 g. at $T°$ C. =							$\times 10^3$ in Cals.	Ref.
		−185	−78	0	110	184	305	444		
Ni	100	16		70[a]			54[b]			282*d*
	700	48		70[a]			75[b]			
Ni	25	8.6	27	23	15				15	282*e*
	200	11	32.5	28	23					
	600	15	33	33	28					
Fe	600	160	0	0			100[c]			282*d*
	500	3.4	0.7	6						282*m*
Cu	500	7.8	18.5	17.5					=1	282*n*
									10	
W	0.5			0.18	0.08	0.11	0.05		8.6	282*p*
MnO	506		0	0		24	39	20		282*h*
MnO-Cr_2O_3	165		23	15		345	364	217	$\lambda\omega = 2$ $\lambda_A = 20$	282*h*
ZnO	400	105	13.1	13	33	68	39		$\lambda\omega = 1.1$ $\lambda_A = 21$	282*q,r*
ZnO-Cr_2O_3	760	228	52	112	137	160	130			282*r*
Cr_2O_3 gel	700	1350	91	22		200	200			282*s*
ZnO-Mo_2O_3[d]	100	8	0	0	0	5	13.5	16.0	$\lambda\omega = 2$ $\lambda_A = 20$	282*t*
NiO-Mo_2O_3[d]	760	59.2	0	0	2.5	36.5	58.3[e]			282*u*
CuO-Cr_2O_3[d]	760	40	3	1		8	16			282*u*
V_2O_3	650			0		10	24.2	22.8		282*u*
Al_2O_3	650			0	0	0	0	6.7		282*v*

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

TABLE XXX — *Continued*

CARBON MONOXIDE

Adsorbent	$P_{mm.}$	Adsorption in cc. per 100 g. at $T°$ C. =								Ref.
		−185	−78	0	110	184	305	444		
Fe	500	27.5	3.7 11.0	0.2 17.0						282*l*
Cu	200	90	30	22	30					282*n*
MnO-Cr_2O_3	150	2250	530			670	320			282*k*
ZnO-Mo_2O_3	600			2.8	0.5		1.5	0.9		282*t*

NITROGEN

	$P_{mm.}$	T = −183	−78	0	100	300	360	600° C.		
Fe	700	24 30	4	1			1 4.6*			282*l* 282*m*
W	1			0.03	0.07	0.53		1.00		282*p*

* t = 396

ured at the given pressures and various temperatures with different gas-adsorbent systems. The existence of a minimum in the adsorption-temperature isobar is evidence of activated adsorption above the minimum, van der Waals adsorption below. In the lower temperature ranges of activated adsorption, owing to the slow velocity of adsorption, equilibrium data are not reached; hence the minimum in the data; the figures on the ascending branch not representing true equilibria. When trustworthy data are available for the two heats of adsorption, λ_ω for van der Waals and λ_A for activated adsorption, these are given in the next to the last column.

In addition to the above data there is an increasing amount of mate-

[282*l*] A. F. Benton, *Trans. Faraday Soc.*, **28**, 213 (1932).
[282*m*] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934).
[282*n*] A. F. Benton, *Trans. Faraday Soc.*, **28**, 209 (1932).
[282*p*] W. Frankenburger and A. Hodler, *Trans. Faraday Soc.*, **28**, 229 (1932).
[282*q*] H. S.Taylor and D. V. Sickman, *J. Am. Chem. Soc.*, **54**, 602 (1932).
[282*r*] H. S. Taylor and C. O. Strother, *J. Am. Chem. Soc.*, **56**, 586 (1934).
[282*s*] H. S. Taylor and J. Howard, *J. Am. Chem. Soc.*, **56**, 2259 (1934).
[282*t*] H. S. Taylor and G. Ogden, *Trans. Faraday Soc.*, **30**, 1178 (1934).
[282*u*] Unpublished data.
[282*v*] H. S. Taylor, *Z. physik. Chem.*, Bodenstein Festband, 475 (1931).

rial dealing with the activated adsorption of hydrocarbons, obtained by Hollings, Griffith and co-workers [282w] and by Turkevich, Howard, and Taylor. [282s, 282x] At lower temperatures, rapid, reversible van der Waals adsorption obtains. In an intermediate range, characteristic for a given gas and surface, there is adsorption which is measurable in speed and involving activation energies. At some of the temperatures employed, gases so adsorbed may be recovered on evacuation. At still higher temperatures, the activated adsorption occurs with increasing velocity, but processes of decomposition and interaction of fragments intrude, and these are revealed in the subsequent desorption processes by differences between the desorbed gas and that adsorbed. Unsaturated hydrocarbons, such as ethylene, show activated adsorption on the surfaces studied in a lower temperature range than the saturated compounds. The activated adsorption of these latter is only revealed by adsorption measurements in the temperature range above 300° and is accompanied by some decomposition.

Water vapor and nitrous oxide are other gases for which activated adsorption has been reported. [282v, 282q, 282z]

Studies of hydrogen adsorption on zinc oxide [282r] reveal that two distinguishable types of activated adsorption occur, one in the region 0–110° C. with a low activation energy of 3–6 kilocals., the other in the range of temperature above 184° with an activation energy of 8–15 kilocals., the intermediate temperature range showing decreasing adsorption with increase of temperature. Similar observations for hydrogen adsorption on iron ammonia-making catalysts, showing two types of activated adsorption, one in the range −90 to 0° C., the other above 100° C., have been made by Emmett and Harkness.[282.1] The detailed examination of hydrogen adsorption on chromic oxide gel catalysts by Burwell and Taylor [282.2] leads definitely to the conclusion that the surface is composite, with areas having characteristic activation energies of adsorption, from low values to a value of 21.7 kilocals. per mol. This latter obtains on an area relatively uniform and large in extent, conveniently studied at temperatures above 180° C.

The range of temperature in which activated adsorption by oxides manifests itself is greatly modified by employing suitable mixtures of oxides. The following table of data from the paper by Taylor and Howard [282s] shows this influence of mixture quantitatively in regard to activation energy.

[282w] H. Hollings and R. H. Griffith, *Proc. Roy. Soc.*, A **148**, 186 (1935).
[282x] H. S. Taylor and J. Turkevich, *J. Am. Chem. Soc.*, **56**, 2254 (1934).
[282v] L. Meyer, *Naturwiss*, **20**, 791 (1932).
[282z] H. S. Taylor and A. J. Gould, *J. Am. Chem. Soc.*, **56**, 1685 (1934).
[282.1] P. H. Emmett and R. W. Harkness, *J. Am. Chem. Soc.*, **57**, 1631 (1935).
[282.2] R. L. Burwell and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 697 (1936).

TABLE XXXI — ACTIVATION ENERGY AND VAN DER WAALS ADSORPTION ON OXIDES AND THEIR MIXTURES

Adsorbent	van der Waals Adsorption of H_2 at 194° K., cc. per g.	Activation energy, Kg. Cal. per g. mol for H_2 adsorption = 0.2 cc. per g.
ZnO	0.2	11
Cr_2O_3	0.7	19
ZnO-Cr_2O_3	0.6	1
MnO	0.1	20
MnO-Cr_2O_3	0.5	6

The accumulation of quantitative data with respect to activated adsorption has raised questions as to the mechanism whereby the process occurs. Some modification of the simple kinetic picture as first formulated by Taylor is doubtless necessary. The data cannot be reconciled with the simple assumption that every gas molecule is adsorbed which strikes the surface with the necessary activation energy. In the expression for the velocity of adsorption $v = Ae^{-E/RT}$ it is evident from the experimental data that, as E increases, the magnitude of A appears also to increase, so that a linear relationship obtains, of the form,

$$\log A = aE + b,$$

where a and b are empirically determined constants. Similar relations obtain between the activation energies and specific activities of catalysts in heterogeneous catalytic reactions (see page 252).[282.3] As Eckell remarks, the interpretation of this relation between A and E is very much a matter for discussion with, as yet, no general agreement. The problem in its adsorption aspects has recently been discussed by Howard,[282.3] Pace and Taylor [282.4] and by Roginsky.[282.5]

Further Criteria for Activated Adsorption: The definition of activated adsorption especially in respect to hydrogen adsorption has been much assisted by the development of our knowledge, first, with respect to the existence of the two forms of molecular hydrogen, ortho- and para-hydrogen and, latterly, with respect to the existence of the hydrogen isotope, deuterium, of mass 2. We shall review this evidence, which provides an excellent illustration of advance in one field assisting developments in a quite different field of research.

[282.3] G.-M. Schwab, *Z. physik. Chem.*, B **5**, 406 (1929); A. A. Balandin, *Z. physik. Chem.*, B **19**, 451 (1932); J. Eckell, *Z. Elektrochem.*, **39**, 859 (1933).

[282.4] J. Pace and H. S. Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

[282.5] S. Roginsky, *Nature*, **134**, 935 (1934).

Activated Adsorption and the Spin-Isomerization of Hydrogen: The experimental demonstration by Bonhoeffer and Harteck [282.6] of the quantum-mechanically predicted two forms of molecular hydrogen immediately aroused interest from the standpoint of surface catalysis, since the method of production of the para-form of the molecule involved conversion at charcoal surfaces at liquid hydrogen temperatures. The reconversion process, para- to ortho-, at higher temperatures, revealed, at first, certain anomalies which invited experimental test. Work by Bonhoeffer and Farkas [282.7] on the reconversion process at electrically heated wire surfaces demonstrated parallelism with the phenomena of heterogeneous catalysis. The correspondence existing between the capacity of surfaces to show activated adsorption and their capacity to catalyze chemical reactions between gases so adsorbed indicated that a similar correlation might apply to the ortho-para hydrogen conversion. From a study of various metals and oxide catalysts, Taylor and Sherman [282.8] concluded that there is a definite parallelism between the activity of a surface in inducing the spin-isomerization of hydrogen and its ability to adsorb hydrogen in the activated form.

This mechanism has since been completely substantiated in the high temperature range where activated adsorption predominates. It soon became apparent, however, that, at low temperatures, where van der Waals adsorption is predominant, the conversion process must be otherwise explained. From the behavior of hydrogen on charcoal at low temperatures where the equilibrium conversion process was found to be independent of pressure and of temperature, as well as from the great acceleration of conversion exerted by oxygen adsorbed on the charcoal at liquid air temperatures, Bonhoeffer, Farkas and Rummel [282.9] came to the conclusion that the adsorbed hydrogen molecules underwent spontaneous transformation from one form to the other without interaction with other hydrogen molecules or hydrogen in any form whatever. They assigned the transformation to the existence, on the charcoal surface, of magnetic dipoles, and, in presence of adsorbed molecular oxygen, to the magnetic effect of this gas.

This mechanism of the low temperature ortho-para conversion involving

[282.6] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, B **4**, 113 (1929).

[282.7] K. F. Bonhoeffer and A. Farkas, *Z. physik. Chem.*, B **12**, 231 (1931).

[282.8] H. S. Taylor and A. Sherman, *J. Am. Chem. Soc.*, **53**, 1614 (1931) *Trans. Faraday Soc.*, **28**, 247 (1932).

[282.9] K. F. Bonhoeffer, A. Farkas and K. W. Rummel, *Z. physik. Chem.*, B **21**, 225 (1933). This paper develops ideas first indicated by Bonhoeffer and Farkas, *Trans. Faraday Soc.*, **28**, 245 (1932).

gases adsorbed by van der Waals forces parallels that shown by L. Farkas and Sachsse with the ortho-para conversion in homogeneous systems when paramagnetic molecules are present.[282.10] These authors observed that, whereas a whole series of diamagnetic gases was without effect, the paramagnetic gases, oxygen, nitric oxide and nitrogen dioxide, as well as dissolved paramagnetic ions for conversion of dissolved hydrogen, were capable of accelerating the ortho-para conversion.

Emmett and Harkness [282.11] reported conversions on iron synthetic ammonia catalysts at liquid air temperatures at velocities which indicated that van der Waals adsorption and not activated adsorption was involved. About the same time, Taylor and Diamond found a more rapid ortho-para conversion on silver at liquid air temperatures than at −78° C., there being a characteristic minimum in the curve for rate plotted against temperature. The observation by Howard and Diamond of extremely rapid conversions on chromic oxide gel at −190° C. once more suggested the conversion of molecularly adsorbed hydrogen by magnetic forces in the surface. Extending these observations, Taylor and Diamond [282.12] secured rapid conversions, with van der Waals adsorption as the predominant adsorption, on paramagnetic rare earth oxides such as gadolinium and neodymium oxides, whereas the diamagnetic lanthanum oxide showed an efficiency lower by several orders of magnitude. Pure ceric oxide exhibited low activity, in agreement with its low paramagnetism. The lower oxide of cerium, probably more highly paramagnetic than the completely oxidized sample, showed higher ortho-para conversion efficiency. Similar relations obtain between vanadium pentoxide and the same element in a lower state of oxidation. Zinc oxide, which is diamagnetic, shows poor conversion efficiency at liquid air temperatures, whereas zinc chromite and chromium oxide gel, both paramagnetic, are extremely efficient agents for the low temperature conversion. Mention has already been made of the high activity of reduced iron synthetic ammonia catalysts. Magnetic oxide of iron shows moderate conversion at liquid air temperatures even though the extension of surface, and hence the van der Waals adsorption, is low. The conversion efficiency is not confined to oxides. Paramagnetic solid salts such as manganous chloride bring about rapid ortho-para conversion.

In the work of Taylor and Diamond [282.12] as well as in that of Bonhoeffer, Farkas and Rummel [282.9] conversion was obtained at low temperatures

[282.10] L. Farkas and H. Sachsse, *Z. physik. Chem.*, B 23, 1 (1933).

[282.11] P. H. Emmett and R. W. Harkness, *J. Am. Chem. Soc.*, **55**, 3496 (1933).

[282.12] H. S. Taylor and H. Diamond, *J. Am. Chem. Soc.*, **55**, 2613 (1933); **57**, 1251 (1935).

on surfaces not ordinarily regarded as paramagnetic. Charcoal is a good example and it was shown that, even in the absence of paramagnetic impurities in the charcoal, good conversion efficiencies are obtained. Silver is a further example, studied by Taylor and Diamond, in which definite if small conversion was obtained in the van der Waals range of adsorption with a pure substance diamagnetic in character. Such activity must be associated with the unsaturated atoms of the surface lattice which must be regarded as possessing magnetic properties.

Evidence for Activated Adsorption of Oxygen: The ortho-para hydrogen conversion may also be used as a criterion of the adsorption of oxygen in two forms, one involving activation energy. We have already noted the evidence of L. Farkas and Sachsse as to the homogeneous conversion of para- to ortho-hydrogen accelerated by paramagnetic molecular oxygen. Oxygen adsorbed on charcoal at liquid air temperatures proves to be still paramagnetic since the gas so adsorbed markedly accelerates the ortho-para conversion. Oxygen adsorbed on charcoal above $-78°$ C. is, however, adsorbed differently and in this condition of adsorption actually retards the conversion process. These data from spin-isomerization confirm beautifully the conclusions from adsorption studies of oxygen mentioned in the introductory paragraph on activated adsorption (p. 204).

General Conclusions Concerning Spin-Isomerization: We can generalize our conclusions concerning spin-isomerization in relation to activated adsorption as follows: (*a*) The ortho-para hydrogen conversion is a convenient index of activated adsorption of hydrogen in the high temperature range when van der Waals adsorption is negligibly small. The results of such studies confirm conclusions based on velocity of adsorption. (*b*) At temperatures where van der Waals adsorption is high, ortho-para conversion is not an index of activated adsorption, since such conversion may be caused by the paramagnetism of the bulk material or by the magnetic characteristics of the surface atoms. (*c*) Spin-isomerization may be utilized to reveal activated adsorption of paramagnetic gases.

The limitations which the paramagnetic properties of solids thus place on the utilization of spin-isomerization as a criterion of activated adsorption are avoided by the development, now to be discussed, of a new criterion of activated adsorption rendered possible by the discovery and isolation of the hydrogen isotopes.

Isotope Exchange Reactions as Criterion of Activated Adsorption: The discovery and isolation of the heavy hydrogen isotope, deuterium (D_2) at once makes possible investigations parallel to those just discussed in connection with spin-isomerization. In place of the determination of

the conversion from ortho- to para-hydrogen, the conversion of a mixture of H_2 and D_2 molecules to the equilibrium mixture of H_2, HD and D_2 molecules may be used as the criterion of activated adsorption. In such studies it is assumed that the isotope reaction in question

$$H_2 + D_2 = 2HD$$

cannot be achieved in adsorbed layers where the binding to the surface is by van der Waals forces. Alternatively, the occurrence of the reaction is assumed to be an index of the existence, on the surface, of hydrogen adsorbed by homopolar binding and requiring an activation energy for such adsorption.

An investigation of this isotope exchange reaction as a criterion of adsorption has been conducted recently by Gould, Bleakney and Taylor,[282.13] using nickel and chromium oxide gel catalysts as catalytic agents. The progress of the exchange reaction was followed by a mass spectrographic analysis of the gas mixture, since the formation of HD molecules leads to the production in the mass spectrograph of diatomic ions of mass 3 in place of those of masses 2 and 4 in the initial mixture. A thermal conductivity method of analysis devised by Farkas and Farkas [282.14] can similarly be employed. The experimental work revealed, quite surprisingly, that, even at liquid air temperatures, the exchange reaction is actually occurring slowly. At $-78°$ C., the rate has become sufficiently rapid that equilibrium was attained under the experimental conditions in one hour. These results indicate therefore that, even in the lower range of temperatures, some of the adsorption occurring is of the activated type. Since equilibrium is established in the gas phase, the rates of adsorption and desorption leading to the exchange equilibrium must be rapid. The desorption process will be the slower of the two and since it is occurring at the low temperatures in question the activation energy of the process must be low and the heat of adsorption (which is included in the activation energy of desorption) must be lower still. Howard and Taylor [282g] found that the activated adsorption of hydrogen on chromium oxide gel as studied by velocity of adsorption measurements was only conveniently measurable at 0° C. and upwards and had a heat of adsorption of $\backsim$25 kilocals. and an activation energy of $\backsim$20 kilocals. It is quite evident therefore that the isotope exchange reaction, $H_2 + D_2 = 2HD$, occurring at surfaces, represents an enormously more sensitive test of activated adsorption than is possible via measurements of adsorption velocities and adsorption

[282.13] Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).
[282.14] A. Farkas and L. Farkas, *Proc. Roy. Soc.*, A **144**, 467 (1934).

isobars and such adsorption may be thus detected even at temperatures where considerable van der Waals adsorption occurs.

In comparison with the rapid conversion of ortho- to para-hydrogen on chromium oxide gel surfaces at liquid air temperatures the isotope exchange reaction at these temperatures is slow. This indicates that the rapid spin-isomerization at liquid air temperatures is not due in any marked degree to activated adsorption but is rather to be ascribed to the magnetic phenomena already discussed. In the higher temperature ranges, where van der Waals and magnetic factors are negligible, there is a complete concordance in the evidence for activated adsorption of the hydrogen as obtained, for example, by Bonhoeffer, Bach and Fajans,[282.15] in studies of ortho-para conversion and isotope exchange at metal surfaces. Activation or poisoning of the metal surface produced similar effects in the two processes. This proves that the mechanism of both processes is the same and occurs via activated adsorption on the metal surface.

Other Exchange Reactions: The study of activated adsorption via isotope exchange is not confined to the hydrogen isotopes alone but may be extended to other hydrogen containing molecules as was demonstrated by Farkas, Farkas and Rideal [282.16] and by Horiuti, Ogden and Polanyi.[282.17] In these cases, ready interaction of ethylene and benzene with deuterium on nickel catalysts was revealed, producing deutero-substituted products as well as addition products. Morikawa, Benedict and Taylor [282.18] showed that the deuterium substitution occurs, but less readily with saturated aliphatic hydrocarbons on nickel catalysts in the region of 100–150° C. Also, interaction between methane and methane-d_4 can be secured at 138° C. and higher. This interaction between isotopic forms of the molecules in question is therefore a much more sensitive index than adsorption measurements of the activation of the molecules at the surface. The ready occurrence of these reactions between saturated molecules points to the existence of dissociative adsorption on the catalyst surface. Taylor and Jungers [282.19] showed that iron ammonia catalysts effect the exchange reaction between deuterium and ammonia even at room temperatures. This definitely indicates that the rate controlling

[282.15] K. F. Bonhoeffer, F. Bach and E. Fajans, *Z. physik. Chem.*, A **168**, 313 (1934).

[281.16] A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc.*, A **146**, 630 (1934).

[282.17] J. Horiuti, G. Ogden and M. Polanyi, *Trans. Faraday Soc.*, **30**, 663 (1934). J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30** (1934).

[282.18] M. Morikawa, W. S. Benedict and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 1445, 1795 (1936).

[282.19] H. S. Taylor and J. C. Jungers, *J. Am. Chem. Soc.*, **57**, 660 (1935).

factor in ammonia synthesis is the activated adsorption of the nitrogen, a conclusion in accord with the results of adsorption measurements by Emmett and Brunauer.[282m]

This use of deuterium in the exploration of activation of specific bonds in complex molecules constitutes an asset of a fundamental character in the general field of surface reactions, permitting a more detailed analysis of the association between reactant and catalyst.

CHAPTER XII

THE KINETICS OF HETEROGENEOUS CATALYSIS

WE shall now turn from a quite definite picture of the adsorption layer to a consideration of chemical processes which occur in this layer, and, more particularly, to the kinetics of catalysis.

The Rate-Determining Processes: As has already been seen in principle (p. 178), the progress of a heterogeneous catalytic reaction consists of at least three steps: the diffusion of the reactants to the catalyst, the chemical change at the surface and finally the diffusion of the reaction products away from the catalyst. To these must be added, as a result of our knowledge of the adsorption process, the formation of the adsorption-compound, catalyst-reactant, after the diffusion is complete, and also the decomposition of the compound, catalyst-product, which must precede the diffusion away from the surface. As has already been set forth, unless they all accidentally possessed the same velocity, it is the slowest of these five processes which determines the velocity since they all follow each other (consecutive reactions). According to Frankenburger,[283] it is the primary problem of catalytic kinetics to distinguish between these five possibilities capable of determining the velocity both as to order of reaction and temperature coefficient.

If, for example, the diffusion to the contact agent is the measured process, the temperature coefficient must be small, corresponding to that of all diffusion processes in gases or liquids, but the velocity must be proportional to the gas (or solution) concentration, and hence, of the first order. If, on the contrary, the formation of the adsorption complex in the surface determines the velocity, the order of reaction remains the same but the temperature coefficient would be, according to Frankenburger, that of a chemical reaction and therefore large. The determination of velocity by the formation of the adsorption complex occurs if the determining adsorption for the reaction is, on the one hand, activated adsorption or if, on the other hand, the rearrangement of the adsorbate in the surface occurs very rapidly. The first alternative occurs, in general, in reactions of hydrogen at hydrogenation catalyst surfaces, metal or oxide, where only activated or atomic adsorption of hydrogen leads to reaction. In spite of this, in the hydro-

[283] W. Frankenburger, *Z. Elektrochem.*, **35**, 278 (1929).

genation of double bonds the rearrangement in the surface is velocity determining [283a] and equilibrium in the activated adsorption is maintained. Indeed, the activation energy required by a double bond to react heterogeneously with adsorbed atomic hydrogen is sufficiently large that,[283a, b, c] in the region of measurable hydrogenation, adsorption equilibrium is maintained. Hence, even in the cases where the catalytically active adsorption is not, as we assumed in the equation on page 186, immeasurably fast and temperature independent, we may, *in general*, neglect the velocity of adsorption as compared with the velocity of the actual rearrangement.[283d]

Only when the rearrangement itself requires no, or a very small, activation can the adsorption of the substrate be rate determining. This is the case in the conversion of para to normal ortho-para hydrogen, because the rearrangement is already complete in the dissociation into atoms and their recombination.[283e] The same is also true in the establishment of equilibrium between the isotopes of hydrogen,

$$H_2 + D_2 = 2HD,$$

because in this case, also, the process is complete after dissociation at the surface and statistical rearrangement. The slowest process is the re-evaporation of the product molecules, the velocity of which is determined by the heats of adsorption and the activation energy of adsorption. Both the para-hydrogen conversion via atoms and the isotope exchange are, except for a small isotope effect, equal in velocity.[283f] In the case of ammonia synthesis the evidence also points to the activated adsorption of nitrogen as the rate-determining process.[283g]

In general, however, in normal chemical reactions, the adsorbate can be regarded as an Arrhenius intermediate (page 72). Then, the order of reaction will normally be first order as in the case of velocities determined by

[283a] G.-M. Schwab and H. Zorn, *Z. physik. Chem.*, B **32**, 169 (1936).

[283b] G.-M. Schwab and Brennecke, *Z. physik. Chem.*, B **16**, 19 (1932).

[283c] E. B. Maxted and Moon, *J. Chem. Soc.*, 1190 (1935).

[283d] See also in this connection: C. Wagner, *Z. physik. Chem.*, A **159**, 459 (1932); B. Topley, *Nature*, 18th July, 1931.

[283e] K. F. Bonhoeffer and A. Farkas, *Z. physik. Chem.*, B **12**, 231 (1931); A. Farkas, *ibid.*, B **14**, 371 (1931); Bonhoeffer and Farkas, *Trans. Faraday Soc.*, **28**, 242 (1932); Rowley and Bonhoeffer, *Z. physik. Chem.*, B **21**, 84 (1933); Bonhoeffer, Farkas and Rummel, *Z. physik. Chem.*, B **21**, 225 (1933); H. S. Taylor and A. Sherman, *J. Am. Chem. Soc.*, **53**, 1614 (1931).

[283f] E. Fajans, *Z. physik. Chem.*, B **28**, 239 (1935); Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

[283g] Emmett and Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934). J. C. Jungers and H. S. Taylor, *J. Am. Chem. Soc.*, **57**, 660 (1935).

the rate of adsorption, and the temperature coefficient will be the normal relatively large one of chemical processes, namely, that of the transformation of the adsorbate. The picture is quite otherwise if the processes of desorption, either the decomposition of the catalyst-product complex or the diffusion of the product from the surface, determine the velocity. In these cases, the order should be zero or reciprocal first order, and the two cases will be distinguished once more by the temperature coefficient in the way discussed for the corresponding processes involving the reactants. In these two last cases, the behavior towards changes in the velocity of gas flow is quite characteristic. Raising the velocity of flow involves an accelerated removal of the reaction products and, thereby, a reaction acceleration.

First, as to the diffusion processes to and from the catalyst, these actually determine the velocity in many practical examples. Especially in technical catalysis, where large conversions in unit time have to be achieved, it is the velocity of gas flow, bringing the reactants to the contact agent and removing the reaction product, that is often the limiting factor. The same is true, also, in general, for heterogeneous catalysis in solutions, in which diffusion is much slower than in gases. In such cases, it can nearly always be assumed that the actual conversion at the catalyst goes so quickly that the diffusion of the substrate to the surface determines the velocity. This diffusion is equivalent to a reaction of the first order. To such processes, the theory is applicable [284] which was worked out by Noyes and Whitney,[284a] Nernst and Brunner [284b] for the velocity of solution of solid bodies.

A special case obtains with extraordinarily microporous catalysts such as are designated ' skeletal contact masses ' which are formed by dissolving one component of an alloy. In the United States the so-called Rainey nickel catalyst is such a contact mass formed from an aluminum-nickel alloy by solution of aluminum. In such cases, the greater part of the catalytic process occurs in the interior of the pseudo-crystallites remaining after the solution process. If this reaction process is rapid, the diffusion of the substrate through the very fine pores of the contact mass into the interior will be rate determining. This process shows all the evidences of a diffusion as outlined above, such as first order and small temperature dependence.[284c]

With all normal heterogeneous gas reactions, however, it is always possible, by suitable experimental arrangements, such as by static methods

[284] G. Bredig and J. Teletow, *Z. Elektrochem.*, **12**, 582 (1906).
[284a] A. A. Noyes and W. R. Whitney, *Z. physik. Chem.*, **23**, 689 (1897).
[284b] W. Nernst and E. Brunner, *Z. physik. Chem.*, **47**, 52, 56 (1904).
[284c] G.-M. Schwab and Zorn, *Z. physik. Chem.*, B **32**, 169 (1932).

using suitable conditions of flow or convection (Hinshelwood, Dohse) or by the use of very low pressure (Langmuir, Schwab-Pietsch, Cassel, Glückauf) to sidetrack the influence of the transport of the gases to and from the surface and to measure the process at the surface itself. It was long believed, largely from the work of Bodenstein and Fink,[285] that this was also a diffusion phenomenon through a layer of adsorbed gas; however, since the recognition of the unimolecularity of catalytic adsorption this is no longer tenable.[286]

Concerning the determination of velocity by the desorption process, a little more may be added. A slow desorption is coupled with an accumulation of the reaction products on the surface. Gradually, therefore, the whole surface will become covered, since the adsorption layer is unimolecular, and, thereby, the reaction itself, which is proportional, not to the surface covered with product, but to the bare surface, will finally become the slowest process of all. The determination of the velocity by desorption, which Frankenburger [283] differentiates from the covering up of the surface, becomes, accordingly, identical with it in the stationary state.

In treating the kinetics of catalytic reactions in the sense of the preceding observations, it will be assumed in every case that adsorption equilibrium obtains for all the reactants and products in the gaseous space, so that the velocity of reaction will be determined in the two-dimensional surface phase by the usual methods. The velocity appears then as a function of the gaseous concentration and all retarding and accelerating effects, which, in flow systems, are caused by changes in the velocity of gas flow, only operate as they may change the concentrations in the gas phase.

Different possible cases will now be considered such as have been studied in recent times by different workers, notably Langmuir, Hinshelwood and others. We shall treat, first of all, simple decomposition reactions, reactions therefore with only one reactant.

I. Reactions with a Single Reactant

1. No Retardation: In these cases, adsorption of the reaction products does not occur, at least on those areas of the surface which bring about the change. The velocity of reaction is, then, simply proportional to the adsorbed amount or to the area of surface covered by the reactants. There are three cases to be distinguished dependent on the strength of the adsorption in the region measured.

[285] M. Bodenstein and C. G. Fink, *Z. physik. Chem.*, **60**, 1 (1907).
[286] M. Bodenstein, *Z. physik. Chem.*, B **2**, 345 (1929).

(*a*) *Weak Adsorption:* The isotherm has the form (page 187),

$$\sigma = bp$$

and, therefore,

$$\frac{dx}{dt} = k'\sigma = k'bp = kp,$$

that is to say, the reaction proceeds simply as one of the first order. This rate is obeyed by the decomposition reactions of such hydrides as AsH_3 on glass,[286a] PH_3 on glass,[286b] HI on platinum,[286c] SeH_2 on selenium,[286d] CH_4 on carbon,[286e] and also the decomposition of nitrous oxide on gold,[286f] and on the basic oxides of the principal groups of the periodic system.[286g]

(*b*) *Moderate Adsorption:* The Langmuir isotherm, in its explicit form, has to be employed:

$$\frac{dx}{dt} = k'\sigma = \frac{kp}{1 + bp}.$$

The decomposition of N_2O on In_2O_3 follows this equation.[286g] The conversion of ortho- to para-hydrogen follows the same kinetics in the adsorption layer at the surface of solid oxygen.[286h] The k constant thus found can, in this case, be quantitatively identified with the homogeneous paramagnetic conversion of ortho-hydrogen and the b constant with a plausible value for the heat of adsorption. Approximately, this expression may be replaced by one of a "fractional" order, thus:

$$\frac{dx}{dt} = kp^n,$$

corresponding to the classical adsorption isotherm (page 193), as used by Stock and Bodenstein [287] to interpret the decomposition of SbH_3, with $n = 0.6$.

(*c*) *Strong Adsorption:* The surface is saturated with reactant at all the pressures prevailing:

$$\frac{dx}{dt} = k'\sigma; \sigma = 1.$$

Hence,

$$\frac{dx}{dt} = k.$$

[286a] Van't Hoff, Etudes de dynamique chimique, p. 83.
[286b] Van't Hoff and Kooij, *Z. physik. Chem.*, **12**, 155 (1893).
[286c] Hinshelwood and Burk, *J. Chem. Soc.*, **127**, 2896 (1925).
[286d] Bodenstein, *Z. physik. Chem.*, **29**, 429 (1899).
[286e] Schwab and Pietsch, *Z. physik. Chem.*, **121**, 189 (1926).
[286f] Hinshelwood and Prichard, *Proc. Roy. Soc.*, A **108**, 211 (1925).
[286g] Schwab, Staeger and v. Baumbach, *Z. physik. Chem.*, B **21**, 65 (1933).
[286h] E. Cremer, *Z. physik. Chem.*, B **28**, 383 (1935).
[287] A. Stock and M. Bodenstein, *Ber.*, **40**, 570 (1907).

This case, which is very characteristic of adsorption catalysis implies that the reaction velocity is independent of the concentration, the reaction being therefore of " zero " order. The decomposition of hydrogen iodide on gold [288] is a quite accurate example of this kind, that of ammonia on tungsten [289] a less ideal case. It is important that practically all hydrogenations in solution obey this equation so far as the hydrogen acceptor is concerned, since these cases occur mainly with the catalyst surface saturated with the substance to be hydrogenated. With small acceptor concentrations the case goes over into case IIb (moderate adsorption), as found by Schwab and co-workers.[289a] At normal hydrogen concentrations on nickel the reaction is zero order [289b]; at smaller concentrations there are deviations in this case also.[289c]

2. Reactions Showing Retardation: As already observed, it frequently happens that a reaction product is so slowly desorbed, that is to say, is so strongly adsorbed, that it covers a portion of the catalytically active surface in equilibrium and so withdraws it from the reaction. The products of the reaction operate analogously to contact poisons (pages 270 et seq.).

(*a*) *Reactant A weakly adsorbed; Product B moderately adsorbed:* The surface free from B is:

$$1 - \sigma_B = \frac{1}{1 + b_B p_B}.$$

On this surface, A, since it shows only weak adsorption, will be adsorbed linearly and without changing $1 - \sigma_B$ by displacement. Hence,

$$\sigma_A = b_A(1 - \sigma_B)p_A = \frac{b_A p_A}{1 + b_B p_B}$$

and

$$\frac{dx}{dt} = \frac{k \cdot p_A}{1 + b_B p_B}.$$

Schwab, Staeger and v. Baumbach find this equation for N_2O decomposition on cadmium oxide [286a] probably also on ZnO [289d] as well as CuO and NiO. Hinshelwood and Prichard [290] employed this equation quite accurately in the case of nitrous oxide on platinum. Unfortunately, measurements at

[288] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 1552 (1925).
[289] C. N. Hinshelwood and R. E. Burk, *ibid.*, **127**, 1105 (1925).
[289a] Schwab, Brennecke, *Z. physik. Chem.*, B **16**, 19 (1932); See also [284c].
[289b] Schwab and Rudolph, *Z. physik. Chem.*, B **12**, 427 (1931).
[289c] zur Strassen, *Z. physik. Chem.*, A **169**, 81 (1934); Schwab, *ibid.*, A **171**, 421 (1935).
[289d] Schwab and Staeger, *Z. physik. Chem.*, B **25**, 418 (1934).
[290] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 327 (1925).

low pressures by Cassel and Glückauf [291] yielded a quite different result, which indicates interaction with and inhibition by adsorbed atomic oxygen. In agreement with this result, measurements by Schwab and Eberle [291a] as well as data of Steacie and McCubbin [291b] show that oxygen formed in the reaction acts more effectively as inhibitor than added oxygen. Schwab and Eberle found the velocity to be difficultly reproducible which was also the experience of van Praagh and Topley.[291c]

Conditions are simpler in the decomposition of NO on platinum where Zawadsky and Perlinsky [291d] find the equation applicable.

(*b*) *Reactant weakly adsorbed, Product strongly adsorbed:* The product B is adsorbed practically up to the saturation limit. Since $b_B p_B$ is now much greater than unity, it is only necessary to leave out 1 from the denominator of the previous equation, which then becomes:

$$\frac{dx}{dt} = k \frac{p_A}{p_B};$$

that is to say, the velocity is now inversely proportional to the pressure of the reaction product. According to Green and Hinshelwood, [292] as well as Zawadsky and Perlinsky, [291d] the decomposition of nitric oxide on platinum, with oxygen as inhibitor B, conforms to this equation; however, according to Bachmann and G. B. Taylor [293] this formulation of the retardation is correct but the numerator and hence the reaction itself is bimolecular, a gaseous nitric oxide molecule colliding with an adsorbed molecule. Between 0.25 mm. and 10 mm. pressure, the decomposition of ammonia on platinum follows the equation strictly,[294] with hydrogen as retarding product B, but at higher pressures an unexplained complication (see page 316) occurs, and at lower pressures retardation by added nitrogen also obtains. The same equation is obtained in ammonia decomposition on iron by Winter [294a] who gives another interpretation for the cases both of iron and platinum.

(*c*) *Reactant and Product are strongly adsorbed:* In this case it is necessary to use the isotherm for mixed gases (page 190) with the exception

[291] H. Cassel and E. Glückauf, *Z. physik. Chem.*, B **9**, 427 (1930).

[291a] Schwab and Eberle, *Z. physik. Chem.*, B **19**, 102 (1931).

[291b] Steacie and McCubbin, *J. Chem. Phys.*, **2**, 585 (1934).

[291c] van Praagh and Topley, *Trans. Faraday Soc.*, **27**, 312 (1931).

[291d] *C. rend.*, 18th Dec. 1933.

[292] G. E. Green and C. N. Hinshelwood, *J. Chem. Soc.*, 1709 (1926).

[293] P. W. Bachmann and G. B. Taylor, *J. Phys. Chem.*, **33**, 447 (1929).

[294] G.-M. Schwab and H. Schmidt, *Z. physik. Chem.*, B **3**, 337 (1929); *Z. Elektrochem.*, **35**, 609 (1929).

[294a] E. Winter, *Z. physik. Chem.*, B **13**, 401 (1931).

that 1 may be neglected in the denominator owing to the strong adsorption. We thus obtain:

$$\frac{dx}{dt} = \frac{kp_A}{b_A p_A + b_B p_B}.$$

According to Constable [295, 296] this is the velocity equation for the dehydrogenation of alcohol vapor on copper. Retention of 1 in the denominator gives an equation interpreting N_2O decomposition on mixtures of $CuO-Al_2O_3$ and on CuO at lower temperatures.

(*d*) *Reactant weakly adsorbed, Two Products, B and C, strongly adsorbed:* The equation is, obviously,

$$\frac{dx}{dt} = \frac{kp_A}{b_B p_B + b_C p_C}.$$

According to Schwab [297] ammonia decomposes on platinum at pressures below 0.25 mm. in agreement with this equation, both hydrogen and nitrogen retarding the reaction.

II. Reaction between Two Reactants

The most important possibilities in a reaction of two reactants with each other will now be considered.

1. No Retardation by Reaction Products. (*a*) *Both gases weakly adsorbed:* The adsorption is linear; the reaction velocity simply follows the mass action law, that is, it is proportional to the partial pressures of the respective gases each raised to the power of the molecular coefficient in the reaction equation. The hydrogen-oxygen reaction on porcelain,[297a] the hydrogenation of ethylene on inactive copper at high temperature [297b] and the bromination of ethylene on glass [297c] obey this equation, e.g., $dx/dt = kp_{H_2}p_{O_2} = k'p_{H_2}p_{C_2H_4} = k''p_{C_2H_4}p_{Br_2}$.

(*b*) *Reactant A weakly, reactant B moderately adsorbed:* The surface free from B is, as in case I 2*a*, covered by A proportional to its partial pressure

$$\sigma_A = \frac{b_A p_A}{1 + b_B p_B}$$

$$\sigma_B = \frac{b_B p_B}{1 + b_B p_B}.$$

[295] F. H. Constable, *Nature*, **117**, 230 (1926).
[296] F. H. Constable, *Proc. Camb. Phil. Soc.*, **23**, 172 (1926).
[297] G.-M. Schwab, *Z. physik. Chem.*, **128**, 161 (1927).
[297a] Bodenstein, *Z. physik. Chem.*, **29**, 665 (1899).
[297b] Grassi, *Nuovo Cim.* (6) **11**, 147 (1916); Pease, *J. Am. Chem. Soc.*, **45**, 1196 (1923).
[297c] Stewart and Edlund, *J. Am. Chem. Soc.*, **45**, 1914 (1923).

Hence, for the whole reaction,

$$\frac{dx}{dt} = k'\sigma_A\sigma_B = \frac{kp_Ap_B}{(1 + b_Bp_B)^2}$$

an expression which, as can be seen, passes through a maximum, with p_A constant, when $p_B = b_B$. Fig. 30 shows this behavior for the interaction of hydrogen and carbon dioxide on platinum with hydrogen at a pressure of 100 mm. and varying carbon dioxide pressure, as investigated by Hinshelwood and Prichard.[298] Similarly, the formation of water which accompanies the hydrogen sulphide formation at the surface of melted sulphur, in contact with an electrolytic gas mixture of hydrogen and oxygen, also behaves thus, as shown by Norrish and Rideal.[299]

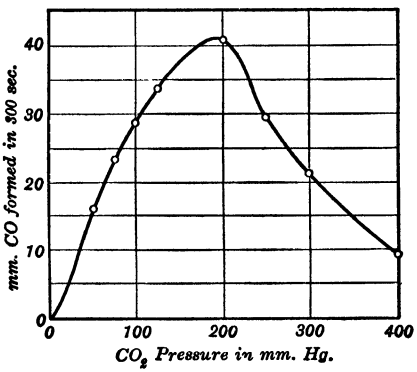


FIG. 30. Influence of Carbon Dioxide Pressure on the Velocity of the Reaction $CO_2 + H_2 = CO + H_2O$ on Platinum. $[H_2]$ = 100 mm.; T = 1273° (Hinshelwood).

(c) *Reactant A weakly, reactant B strongly adsorbed:* Since $b_Bp_B \gg 1$ the equation simplifies to

$$\frac{dx}{dt} = \frac{kp_A}{p_B}$$

that is to say, the maximum is shifted to immeasurably small pressures of B, which retards its own reaction throughout, by displacement of its partner from the surface. For example, according to the fundamental investigations of Langmuir,[300] oxygen behaves thus towards hydrogen and carbon monoxide towards oxygen, at platinum surfaces, at least at temperatures below 700° K. A series of other catalysts show this same behavior.[300a]

(d) *The gas with the smaller partial pressure not markedly adsorbed:* At higher temperatures in the preceding cases, the gas with the lower partial pressure, not markedly adsorbed, collides with a frequency which is proportional to its partial pressure on a saturated layer of the gas in excess, which latter, therefore, does not influence the velocity equation

$$\frac{dx}{dt} = kp_A \quad \text{or} \quad k'p_B.$$

[298] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 806 (1925).

[299] R. G. W. Norrish and E. K. Rideal, *J. Chem. Soc.*, **123**, 1689 (1921).

[300] I. Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1922).

[300a] M. Bodenstein and Ohlmer, *Z. physik. Chem.*, **53**, 166 (1905) for $CO + O_2$; Pease, *J. Am. Chem. Soc.*, **45**, 1196 (1923) for $H_2 + C_2H_4$ on active copper.

Both the Langmuir reactions discussed above show this behavior above 700° K.

(*e*) *One reactant is hydrogen, which dissolves in the metallic catalyst:* In this case A can remove B but B cannot remove A from the catalyst because the hydrogen, owing to the reservoir of gas within the metal, is present at the surface in a density which depends only on its pressure. The kinetic equation is, therefore:

$$\frac{dx}{dt} = \frac{kb_B b_A p_A p_B}{1 + b_A p_A + b_B p_B}$$

which reproduces the hydrogenation of ethylene or nickel over wide ranges of pressure.[289c, 284c] The above expressions are approximations of this equation, which also gives a temperature optimum for hydrogenation.

2. Retardation by the Reaction Products: The only case of this kind studied is the synthesis of sulphur trioxide on platinum, the contact sulphuric acid process. This reaction is, also, at the same time, one of the most difficult problems of heterogeneous kinetics. According to the measurements of Bodenstein and Fink [285] it follows an equation which, for a ratio of sulphur dioxide to oxygen greater than 1.5, has the form:

$$\frac{dx}{dt} = \frac{kp_{O_2}}{p_{SO_3}} \quad \text{or} \quad \frac{kp_{O_2}}{1 + bp_{SO_3}}$$

whereas, with more oxygen, p_{SO_3} enters the numerator in place of p_{O_2}. The assumption of a simple displacement by adsorption would require quite another behavior, namely,

$$\frac{dx}{dt} = \frac{kp_{SO_2}p_{O_2}}{1 + b_1 p_{SO_2} + b_2 p_{O_2} + b_3 p_{SO_3}}$$

where, at the most, one or other term in the denominator would drop out owing to its small value.

The old explanation of Bodenstein and Fink (loc. cit. p. 222), according to which sulphur trioxide covered the surface with a multimolecular layer whose thickness is proportional to $\sqrt{p_{SO_3}}$, the velocity determining process being the diffusion of the more slowly diffusing gas through this layer, gave a completely satisfactory picture, especially as the ratio 1.5, at which the transition from one equation to the other occurs, is actually about the ratio of the diffusion coefficients of oxygen and sulphur dioxide.

On the basis, however, of the recognition of the unimolecular nature of the adsorption layer, this explanation seems to have become untenable. Quite recently, Bodenstein [286] succeeded in bringing the explanation once more within the framework of the two-dimensional surface layer, by pro-

posing that the diffusion process occurs not to the surface but over the surface to the active centers. In particular, if these active centers are, as Schwab and Pietsch assumed,[252] the linear boundaries of inactive areas, the new concept of Bodenstein is quite satisfactory. A necessary modification of the concept has been proposed by Schwab and Pietsch.[252]

Adsorption Equilibrium in Reaction Kinetics: In practically all the cases treated hitherto, with the exception of this last, and perhaps also of the reactions of carbon monoxide and of hydrogen with oxygen on platinum (page 227), concerning which a reference may be made to an interpretation of Eucken,[301] the concept of the adsorbate as the Arrhenius intermediate stage has proved to be completely satisfactory, adsorption equilibrium continuously obtaining and the surface conversion determining the reaction. The other concept of an adsorption process as the rate-determining factor and of a reaction governed by an aliquot portion of the collisions from the gas phase, has not been disproved. In this respect these reactions are analogous to the cases of homogeneous reactions already discussed (see page 71). Schwab and Pietsch [252] specifically show this. Indeed, this latter method of approach has been applied with success, by different people, to catalytic problems and especially by Constable.[295, 296, 302] In his equations, his "lifetime of the adsorbate on the active centers" is actually equivalent, so far as calculations are concerned, with the adsorption coefficient, b. The difference consists in this, that Constable allows an exchange of position of the adsorbed molecules only via the gas phase, whereas in our concept, this may occur, following Volmer, on the surface.

That the assumption of an adsorption layer in equilibrium is not only no objection to the general concept, as Sauter[229] believes, but, on the contrary, is in complete agreement with actual conditions in a typical series of cases, has recently been directly demonstrated by Dohse, in part with Kälberer,[303] in a number of beautiful researches. Dohse has followed kinetically the decomposition of alcohols into olefines and water at the surface of aluminum oxide. The velocity decreases with increasing conversion, not, however, because it is proportional to the alcohol pressure, but because the water formed produces a retardation by displacement. If one removes the water continuously from the gas phase by means of barium oxide, the velocity is strictly of zero order. This corresponds, according to the present point of

[301] Lehrbuch der Chemischen Physik, p. 628, 3rd Edition, Leipzig (1930).

[302] F. H. Constable, *Proc. Camb. Phil. Soc.*, **23**, 176, 593 (1926).

[229] *loc. cit.*, p. 203.

[303] H. Dohse and H. Kälberer, *Z. physik. Chem.*, B **5**, 131 (1929); H. Dohse, *ibid.*, B **6**, 343 (1929); B **8**, 159 (1930); *Z. Elektrochem.*, **36**, 677 (1930).

view (page 223) to case I 1c, to the reaction of a continuously saturated adsorption layer of alcohol.

It should be possible to demonstrate the correctness of this view by preventing the re-establishment of the saturated layer. This can be achieved because the adsorption of the alcohol is so strong that, even at quite low pressures, the surface layer remains practically saturated, as was separately determined. If, therefore, the vapor phase remaining after saturation of the surface be pumped off, the adsorption layer is obtained without external complications, and with no possibility of collisions from the gas phase. The reaction of such surface layers was therefore followed by pressure measurements of the olefine produced. It was found that the reaction follows the equation of the first order, that is to say, the adsorption layer as such reacts proportionately to the extent of surface covered, according to the equation,

$$\frac{dx}{dt} = -\frac{d\sigma}{dt} = k'\sigma.$$

These observations could also be established with identical results for isopropyl, *n*-propyl, secondary and tertiary butyl alcohols as well as for the dehydrogenation reaction,

$$CH_2O = CO + H_2,$$

on zinc oxide surfaces. The ortho-para conversion at low temperatures on charcoal also follows this equation.[303a] The decomposition of a previously established equilibrium adsorption layer is thus directly demonstrated, and it will be well to generalize the assumption so long as there are no examples which contradict it. It may be that contrary cases will be observed but, under normal conditions, this is not very probable, as was emphasized in the introduction to this section.

A further group of velocity equations must now be considered which are only understandable with the aid of an additional concept. We refer to reactions between adsorbed gases which do not exercise a displacement effect on each other.

III. Reactions between Two Gases, both Adsorbed, without Mutual Displacement

Only those cases will be selected which have been studied, found to be free from objection on the score of experimental technique, and for which no other interpretation than that here given seems possible. With moderate

[303a] Rummel, *Z. physik. Chem.*, A **167**, 221 (1933).

adsorption of the two gases, and without mutual displacement, the velocity equation has the form,

$$\frac{dx}{dt} = \frac{kp_A}{1 + b_A p_A} \cdot \frac{p_B}{1 + b_B p_B}.$$

The reactions in question are: $H_2 + N_2O = H_2O + N_2$ on gold, studied by Hutchinson and Hinshelwood [304] and $H_2 + CO_2 = H_2O + CO$ on tungsten, studied by Hinshelwood and Prichard.[305] In the second reaction, at higher pressures, there exists a small mutual displacement.

The additional assumptions must be made, that the catalyst is composed of two types of surface, each of which adsorbs one gas, and that the reaction occurs at the boundaries of the two surfaces proportionally to the product of the two " two-dimensional " concentrations.

Quite a number of reactions can be considered as limiting cases of this equation [305a] but none of them have been so fully studied nor are they so unequivocal as the two mentioned.

Varied Activity of Fractional Surface Areas: A very important point has here been reached. Not only must it be concluded in this case that, for a given reaction, two different types of surface are active on a single metal, but there are also kinetic indications that one and the same catalyst is not always active with the same kind of fractional area of surface in different reactions. The behavior of platinum is indicative of this. We saw that the decomposition of ammonia (see page 225) occurs on this metal at low pressures on a surface which adsorbs hydrogen and nitrogen equally well and practically to complete saturation; the same decomposition at moderate pressures takes place on a surface which only adsorbs hydrogen. The first-named type of surface does not operate at moderate pressures because it is already completely covered with the retarding gases, whilst the second type of surface does not function at low pressures because it is not sufficiently active. Both types of surface are, on the contrary, to be considered as inactive in those reactions catalyzed by platinum in which hydrogen is produced without being considerably adsorbed, as in the hydrogen iodide reaction studied by Hinshelwood and Burk,[306] the carbon dioxide reduction,[293] the electrolytic gas reaction [300] and the reduction of nitrous oxide.[307]

There are, thus, a number of cases, which might be increased by a more extended development of the subject, from which, by a comparison of re-

[304] W. K. Hutchinson and C. N. Hinshelwood, *J. Chem. Soc.*, 1556 (1926).
[305] C. R. Prichard and C. N. Hinshelwood, *ibid.*, **127**, 1546 (1925).
[305a] Schwab, *Erg. exakt. Naturwiss.*, **7**, 276 (1928).
[306] C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 2896 (1925).
[307] C. N. Hinshelwood, *Proc. Roy. Soc.*, A **106**, 242 (1924).

action kinetics, the same conclusion is reached that has already resulted from the study of adsorption and of heats of adsorption, namely, that the catalytic surface is not homogeneous but consists of varying types of surface. The phenomena of poisoning (page 270) and of selective catalysis (page 263) will yield still further indications in this direction.

Whilst adsorption measurements permitted this conclusion to be reached, the kinetic measurements permit the more precise conclusion that, for each individual reaction, the active portion of, or places on, the surface have properties which are alike among themselves. This follows from the observation that we can represent a reaction in its complete course with varying area of surface covered with a single constant b and a single constant k, and therefore with a constant adsorption capacity and a constant catalytic activity.

How this is to be understood in view of the progressive differences in the types of surface areas can first be realized by a consideration of the energy relations of the surface (page 284 et seq.). Here, however, reference will briefly be made to an experiment that can be performed indicating this conclusion from kinetics directly. There are indeed, besides the reactions of Type III already discussed, and the phenomena obtaining with heterogeneous mixed catalysts (page 304), a number of observations, which lead one to the belief that the homogeneous regions which act catalytically are not areas of plane surfaces but are their linear boundaries, and therefore the crystal edges and boundaries of the crystals. Felman and Adhikari [251] have shown that the combination of mercury with iodine vapor does not occur on the whole surface of a mercury droplet but can be shown to occur only at the phase boundary, $Hg-HgI_2$. From the remainder of the mercury surface iodine evaporates as molecules. Benton and Emmett [308] and Larson and Smith [309] also find that the combination of electrolytic gas on nickel and copper does not take place on the whole surface but only at the boundary metal-metal oxide. Similarly, the catalytic decomposition of hydrogen peroxide, the beautiful example of " pulsating catalysis," is localized, according to Bredig and his co-workers,[310] at the waxing and waning boundary between mercury and its layer of peroxide.

Schwab and Pietsch [252] therefore undertook the task of testing the concept, that, in general, the catalytically active positions are such boundary lines between chemically or crystallographically different areas of surface.

[308] A. F. Benton and P. H. Emmett, *J. Am. Chem. Soc.*, **46**, 2728 (1924).

[309] A. T. Larson and F. Smith, *ibid.*, **47**, 346 (1925).

[310] G. Bredig and A. Stark, *Z. physik. Chem.*, B **2**, 282 (1929); A. Antropoff, *ibid.*, **62**, 513 (1908), which gives additional references.

In particular, they have shown that such a concept does not contradict the kinetic equations derived in the preceding sub-sections, in that the concept of " adlineation " on active lines leads to the same conclusions as adsorption on a surface according to Langmuir. At a subsequent stage, further arguments relative to the energetics of the surface and in favor of this concept will be learned. How far a generalization of the findings just mentioned is legitimate can first really be decided on the basis of further experimental material.

CHAPTER XIII

ACTIVATION AND THE MECHANISMS OF CATALYSIS

HITHERTO, we have proceeded on the assumption that the substrate undergoes catalysis by an increase in its readiness to undergo change, due to its adsorption on the catalyst, and we have found this assumption to be confirmed from the standpoint of reaction kinetics. In what this change of the substrate consists, as compared with its free state, has remained an open question.

There are, in principle, many ways of approaching this problem. The most obvious one seems to be the direct measurement of the energy of the surface processes, drawing conclusions from the energy effects observable, especially in the adsorption phenomena. We saw, however, that this direct method can, unfortunately, only yield, in general, qualitative conclusions, owing to the inhomogeneity of the catalyst surface, because the measurements give an average value of a number of areas of which only a small fraction are markedly catalytic. The second method should, therefore, be to study the energy relations at just these active areas. Unfortunately this is only possible indirectly, since the study of the velocity itself, and especially its dependence on temperature, can alone give reliable information concerning the prevailing kinetically active areas. Nevertheless, much has already been obtained in this manner. The third method consists in applying to the problem of catalysis other facts of physics and chemistry, and more recently of theoretical physics, and new observations not kinetic in nature. This last method of approach is, in the main, a problem for the future.

TEMPERATURE COEFFICIENT AND ACTIVATION ENERGY

We shall first discuss the second of the methods mentioned, the energetic interpretation of kinetic measurements at the catalytic surface. For the homogeneous reaction in the two-dimensional gas of the adsorption layer we shall assume the same laws as apply to the homogeneous reaction in three-dimensional gases, namely the Arrhenius equation,

$$k' = s \cdot e^{-E/RT}$$

where E denotes the activation energy of the reaction, s a constant which,

in bimolecular reactions, is the collision number, in unimolecular reactions the conversion probability of the activated molecule, and which also contains factors for the degrees of freedom of the molecule (see p. 10). For homogeneous gas reactions it is now possible, in some few cases, to give a fairly theoretical value for s; for heterogeneous reactions this is not yet possible, although there is no ground for assuming that it is determined by other major factors.

The principal difficulty is that no data can be obtained for the active area of the surface (see p. 283 later) which appears in the constant term, s. On the assumption that, with wire surfaces, the whole geometric surface is active (see, however, p. 284), Topley attempts [310a] to evaluate s on the assumption that, instead of the collision number of unimolecular reactions, the vibration frequency of an atomic vibration (10^{-12} sec.) is to be used. He obtains thereby, in six favorable cases, agreement with experiment. Generally, however, the absolute velocity of a given reaction on a given catalyst material is subject to very large variations (see p. 317). Therefore, the activation energy, E, cannot generally be obtained in heterogeneous reactions from a single k' measurement but only from the differential form of the Arrhenius equation from which the constant, s, is eliminated.

$$\frac{d \ln k'}{dT} = \frac{E}{RT^2} \quad \text{or} \quad \frac{d \ln k'}{d(1/T)} = -\frac{E}{R}.$$

The determination of the temperature coefficient is, therefore, the source of the determination of E. Catalytic reactions are not different in this respect from spontaneously occurring homogeneous reactions.

It must be observed, that the relationship involves k', which, as shown on pp. 223 and 230, connects the velocity with the density of adsorption. Usually, however, the constant measured is k, which relates the velocity to the gas pressure or concentration of solution. An exception is the example studied by Dohse [303] already discussed. The temperature dependence of k cannot, without modification, be evaluated to give the activation energy in the adsorbate. This would involve the same error as when, in a reaction in solution, use was made, not of the concentration in the solution, but of the saturated vapor pressure of the dissolved substance, in order to evaluate k and thence to calculate the activation energy from $d \ln k/d(1/T)$. It can easily be seen that the result would thereby be in error by the temperature coefficient of the solubility, and therefore by the heat of solution. We must, therefore, investigate first the different types of heterogeneous catalysis as to the significance of their temperature coefficients.

[310a] B. Topley, *Nature*, July 18, 1931.

Apparent and True Activation Energies: For this purpose we define the " apparent activation energy," E_a, which is connected with the temperature variation of the measured k, by means of the equation

$$\frac{d\,ln\,k}{dT} = \frac{E_a}{RT^2}.$$

There are, now, three simple cases in which the relation between E_a, so measured, and the desired E is quite clear. The first is the case designated I, 1*c*, the reaction of zero order, in which the reaction velocity is independent of gas pressure, where actually it was found that

$$\frac{dx}{dt} = k'; \quad \sigma = 1; \quad k = k'$$

in this case, therefore,

$$E = E_a,$$

that is to say, the true activation energy is given directly by the measured velocity. This depends upon the fact that the area of surface covered, being saturated, is independent of the temperature. The activation energy of ammonia decomposition on tungsten [289] is known to be 39 kilocals., and that of hydrogen iodide decomposition on gold [288] to be 25 kilocals., because they are reactions of this type. It is noteworthy that, in homogeneous systems, the activation energy of the first reaction is certainly more than 90 kilocals. (it must be so high since k is immeasurably small), that of the second is 44 kilocals. A diminution of the activation energy has resulted due to the catalyst. We shall return to this point later.

If, on the contrary, the reaction occurs according to the first order (Case I, 1*a*), we have

$$\frac{dx}{dt} = k'\sigma; \quad \sigma = bp; \quad \frac{dx}{dt} = k'bp; \quad k = k'b.$$

Now, the surface area covered varies with the temperature and, hence, E is different from E_a. By differentiation of the equation of page 187 we obtain

$$b = \frac{k_1}{k_0} \cdot e^{\lambda/RT}$$

$$\frac{d\,ln\,b}{dT} = -\frac{\lambda}{RT^2}.$$

Hence it follows that:

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} = \frac{d\ln k'}{dT} + \frac{d\ln b}{dT} = \frac{E}{RT^2} - \frac{\lambda}{RT^2}$$

whence

$$E_a = E - \lambda.$$

The apparent activation energy is therefore, in this case, less than the true activation energy by the heat of adsorption of the reacting substance. A large part of all the measured activation energies of first order reactions thereby lose their direct significance. The initial heats of adsorption here in question presumably cannot be directly determined on account of the decrease in heats with increased adsorption. In favorable cases they may, however, be small compared with the activation energy itself.

Occasionally, the lowering of the apparent activation energy can even go so far that it becomes negative, that is to say, the velocity falls with rising temperature. This is the case for all hydrogenations on metal contact masses when the reaction Type II 1*e* goes over into II 1*a* at higher temperatures, because the values of *b* fall.[283c, 284c and 289c] This means that, with rising temperature, the increasing reactivity of the adsorbate is offset by the more rapidly decreasing density of adsorption.

Thirdly, a theoretically similar definite conclusion can be reached in the case of retardation by a strongly adsorbed reaction product or poison.[302] This is Case I, 2*b*, the equation for which is

$$\frac{dx}{dt} = k'\sigma; \quad \sigma = \frac{b_A p_A}{b_B p_B}; \quad \frac{dx}{dt} = k\frac{p_A}{p_B}; \quad k = k'\frac{b_A}{b_B}.$$

Correspondingly, it follows that:

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} = \frac{d\ln k'}{dT} + \frac{d\ln b_A}{dT} - \frac{d\ln b_B}{dT} = \frac{E}{RT^2} - \frac{\lambda_A}{RT^2} + \frac{\lambda_B}{RT^2},$$

whence:

$$E_a = E - \lambda_A + \lambda_B.$$

In this case, the apparent activation energy is increased by the heat of adsorption of the reaction product. Polanyi [311] considered this case of the desorption process involving an expenditure of energy when the reaction is considered from the gas phase. The exact derivation of the three cases treated is due first to Hinshelwood.[12]

Experimental Data: The increase of the apparent activation energy due to retardation is shown definitely, for example, in the hydrogenation of

[311] Polanyi, *Z. Elektrochem.*, **27**, 143 (1921).

ethylene on copper studied by Pease and Harris,[312] where the activation energy of the retarded reaction is 13.4 kilocals., but, at 100° C., where the retardation is decreasing, the value is 12.2 kilocals. and less. The same limitation on the significance of the measured activation energy exists here, as in the previous case. It is, however, possible, as already mentioned, that the corrections may not be very important; thus, the apparent activation energies of the decomposition of ammonia on various metals on which they react sometimes with, sometimes without retardation, are not very different. The measurements of Hinshelwood and Burk, Kunsman, Schwab, Schmidt and others show the following mean values:

TABLE XXXII — ACTIVATION ENERGIES OF AMMONIA DECOMPOSITION

Metal	Pt-W Mixture	Mo	Fe	Ni	W	Pt
E_a	36	36	40	40	42	44 kilocals.

Possibly, however, there exists a compensation of E and λ with one another in these cases also.

The attempt has also been made to demonstrate this relationship by the use of direct calorimetric adsorption measurements. The case is that of the decomposition of alcohols on bauxite, already mentioned (page 229). Dohse [303] has, as previously stated, measured firstly the reaction retarded by water vapor and then the unretarded reaction with continuous removal of the water vapor, the latter reaction being of zero order. The activation energy is thereby considerably reduced and is equal to that which is obtained from the directly observed reaction of the adsorption layer itself (page 230). It can therefore be regarded with certainty as the true activation energy, E. Dohse's values are the following:

TABLE XXXIII — ACTIVATION ENERGIES OF ALCOHOL DEHYDRATIONS

Substrate	E_a retarded kilocals.	E true kilocals.	Difference kilocals.
n-Propyl alcohol	41	28 5	12.5
i-Propyl alcohol	39	26	13
n-Butyl alcohol	44	28	16
sec-Butyl alcohol	36	24	12
tert-Butyl alcohol	—	20	—

The values of the last column should according to the theory represent, with all the alcohols, the heat of adsorption of water on the aluminum ox-

[312] R. N. Pease and C. A. Harris, *J. Am. Chem. Soc.*, **49**, 2503 (1927).

ide. Actually the author's calorimetrically measured values for λ_{H_2O} also lie between 13 and 16 kilocalories. The agreement with the last column of the table is, therefore, as good as could be expected in view of the experimental variations of the direct adsorption measurements.[312a]

Activation Energy in Reactions Kinetically Complex: In all cases in which the reaction velocity cannot be expressed by a simple power of the concentrations of the reacting substances, and for which, therefore, a Langmuir isotherm in its complete form must be employed, no simple relations exist between temperature coefficient and activation energy. While, in the three cases cited, the initial velocities or the half-life periods at equal initial pressures may be substituted for the constants k, in the Arrhenius equation (since k is involved in the first and $1/k$ in the second as sole temperature-dependent factors) this is no longer possible with the more complex cases. It is easy to convince oneself that for cases such as I 1*b*, I 2*a*, or III the so-called "gross activation energies" thus obtained must be, in reality, very complex and inconstant quantities which contain partial pressures and adsorption coefficients.

On the other hand, there is the possibility, even in these cases, of determining by exact kinetic measurements the constants k and b separately for each temperature and so to derive, also separately, both the activation energy and the heats of adsorption, the latter, too, for the active area of the surface. An effort in this direction has been made by Cassel and Glückauf,[291] by calculating, from the decomposition of nitric oxide on platinum, the heat of adsorption of the oxygen atom. Unfortunately, however, the kinetic factors in this reaction are not yet quite definite (see page 225).

[312a] Some uneasiness concerning the agreement here found has been expressed by H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 595 (1931). It should be noted that the retarded reaction is first order with respect to alcohol and, hence, the relationship between true and apparent activation energy is that given in the preceding example $E_a = E - \lambda_{Alc.} + \lambda_{H_2O}$. Granting this, the last column of the table should not be numerically equal to λ_{H_2O} but should equal $\lambda_{H_2O} - \lambda_{Alc.}$ Now the latter was also determined and found to be equal to approximately 20 kilocals. which, to yield agreement with the last column difference, would involve a heat of adsorption for water $\lambda_{H_2O} = 35$ kilocals. Taylor points out that the value for $\lambda_{H_2O} = 13$ to 16 kilocals. found by Dohse is hard to reconcile with the value found for $\lambda_{Alc.} = 20$ kilocals., when it is remembered that the water inhibits the access of alcohol to the surface. It is difficult to see why a substance with a lower heat of adsorption should inhibit the access of a more strongly adsorbed substance (i.e., higher heat of adsorption). Taylor prefers to believe that a heat of adsorption of water in the neighborhood of 35 kilocals. is more in accord with the other data and with the behavior of water kinetically. He points out that this may be one of the cases in which the activation energy of adsorption is playing a part in the determination of the temperature coefficient of the reaction. Tr.

On the contrary, such an evaluation has been successful in the decomposition of nitrous oxide at cadmium oxide and indium oxide surfaces [286g] and at copper oxide and copper oxide-alumina surfaces.[289d] Also the hydrogenation of ethylene on skeletal contact masses [284c] can be similarly evaluated. In the latter case, the determination of the kinetic heats of adsorption for the active centers first made it possible to disentangle the complexities of the reaction and permitted the determination of the true activation energy.

Decrease in Activation Energy of Catalyzed Reactions

The importance of the energy magnitudes, obtained by the processes discussed in the preceding section, in the problem of reaction acceleration may be illustrated by the following considerations. In the equation,

$$k' = Ze^{-E/RT}$$

which represents quite generally a chemical reaction velocity and whose significance was last discussed on page 234, there are indeed two values which may be responsible for the influence of the catalyst, the Z factor and the E factor. An increase of Z, the collision number, say by adsorption, would naturally imply an acceleration of reaction in the adsorption layer. Since the time of Döbereiner, the action of catalysts has been associated with the compression of the substrate in the adsorption layer. A simple consideration, due to Polanyi,[311] shows, however, that this influence is not the more important. The compression due to adsorption is given by the equation discussed on page 197,

$$\frac{N_{\text{ads}}}{N_{\text{gas}}} = \text{O} \cdot v \cdot e^{\lambda/RT}.$$

With a surface of 1 square cm. per cc. and with a unimolecular layer, O is approximately 10^{-8}. (O must express the ratio of the adsorption volume, that is, surface times thickness of layer (10^{-8} cm.), to the gas volume, since it must be a pure number.) The factor v as was seen on page 200, does not change much for various states, even for the gaseous state, and can therefore be approximately set equal to unity. With a heat of adsorption of 5 kilocals., which, for van der Waals adsorption of molecules, with ordinary gases, is a maximum value on porcelain, and at a temperature of 900° abs. the expression accordingly becomes:

$$\frac{N_{\text{ads}}}{N_{\text{gas}}} = 10^{-8} \cdot e^{\frac{5000}{1800}} = 10^{-6.8}.$$

Since the adsorption volume is 10^{-8} times as small as the gas volume the compression is $10^{1.2}$ fold. A trimolecular reaction such as the reaction of electrolytic gas would be accelerated $10^{3(1.2)} = 10^{3.6}$ fold, if only the collision number came into consideration. Experiments of Bodenstein [313] show, however, that, under the given conditions, the acceleration by porcelain is $10^{7.3}$ fold. The mere increase of collision number by compression is thus several powers of ten less than the catalytic acceleration produced. With other reactions, which do not measurably proceed without catalyst, or occur catalytically at lower temperatures, the disagreement is still more pronounced.

Hence, one is led to the conclusion that the important effect of the catalyst is to be ascribed to a change in the value of E. Actually, an increase of the velocity k' indicates a lowering of the activation energy. A decrease of 30 kilocals. in the example already cited would suffice to increase the sensitive exponential factor to the requisite degree.

Physical Interpretation of Decrease in Activation Energy: The next question is how the lowering of the activation energy in comparison with that of the uncatalyzed reaction is to be thought of physically. It is at once clear that the adsorption in itself does not signify an activation, that the heat of adsorption does not serve as an excitation of the substrate. This heat is thermometrically liberated, the adsorbate, is, therefore, in every case, lower in energy than the free gas (or dissolved substance). This is true even if the actual work of the forces of adsorption is split up into an amount of heat liberated and an increase in the internal energy of the molecules, as was assumed by Taylor and Kistiakowsky.[263] It is also true if activation is necessary in the adsorption process. Even in such case, the adsorbed state is at a lower energy level and the exothermic adsorption is not identical with an activation, as Palmer [314] has indicated. Thus, activatedly adsorbed hydrogen in a hydrogenation process can require an activation energy of 20 kilocals.[284c] although the activation energy of adsorption itself has required 10 kilocals.[314a] The adsorption, therefore, operates in such a way that the adsorbate (even, if, according to Taylor, it is in the activated form, that is to say, adsorbed in a suitable form) is so changed that a new activated state can be attained requiring less thermal vibrational energy. This conclusion, which was first stated explicitly by Polanyi,[311] is schematically represented by the following diagram of the energy levels which the system has to pass through in the homogeneous and heterogeneous reactions.

[313] M. Bodenstein, *Z. physik. Chem.*, **29**, 665 (1899).
[314] W. G. Palmer, *Proc. Roy. Soc.*, A **115**, 227 (1927).
[314a] R. Klar., *Z. physik. Chem.*, A **174**, 1 (1935).

It can be seen that the activation energy of the homogeneous reaction (5) is lowered on the surface to the smaller value (2) and that this decrease, apart from the corrections due to the heat of adsorption liberated (1), is principally caused by the high heat of adsorption of the activated state. The resulting concept of the action of the contact agent may thus be expressed: The energy-barrier, E, to be overcome, is lowered in the adsorption

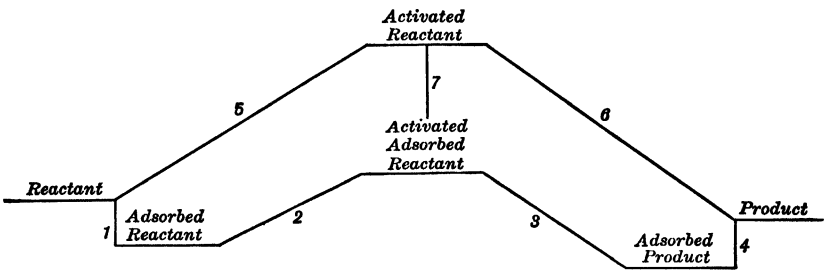


FIG. 31. Energy Levels in Heterogeneous Catalysis.

5–6 Heat of reaction.
2–3 Heat of reaction while adsorbed.
1 Heat of adsorption of reactants.
4 Heat of adsorption of products.
5 Homogeneous energy of activation.
2 True heterogeneous energy of activation.
7 Heat of adsorption in the activated state.

layer because the activated state is strongly adsorbed and, therefore, in the adsorption layer, is less endothermic and therefore more often reached. Hence, it is not that the adsorbate is activated but that the adsorbate is easily activated and is therefore, at equilibrium, present in the activated state to a greater percentage extent than in the free gas.

Naturally, this is only a stricter formulation of the fact that adsorption changes the molecules. Fundamentally, the whole adsorbate is only completely activated when the energy quantity (2) is equal to zero. Hence, the assumption that hydrogen is ionized on metals, as Coehn has demonstrated,[315] must actually be expressed thus: The energy liberated by the passage of electrons and protons into the surface would be so great, owing to the dissociating forces of the metal,[316, 317] that adsorbed hydrogen is split up with very small or no expenditure of energy and is thereby dissociated completely, or practically completely, into these constituents (see page 254).

There arises now the further question, why the activated substrate is so strongly adsorbed. To answer this question is to determine the nature

[315] A. Coehn, *Z. Elektrochem.*, **35**, 676 (1929).

[316] O. Schmidt, *Z. physik. Chem.*, **118**, 193 (1925); A **165**, 133, 209 (1933); *Z. Elektrochem.*, **39**, 824 (1933); *Ber.*, **68**, 1098 (1935).

[317] K. Bennewitz and P. Günther, *Z. physik. Chem.*, **111**, 257 (1924).

of the active intermediate state of the heterogeneous catalytic reaction. Polanyi himself [311] formulated the activated state as the atoms or radicals of the substrate completely free from one another. Their high adsorption is easily understood owing to the "free valences" which they possess. Expressed otherwise, the strong dissociation into atoms of adsorbed molecules is understandable because the free atoms, after their chemical binding (adsorption) on the adsorbent, are at a lower energy level than in the gas.

With the help of rough estimates for the heats of adsorption of the atoms in question, Polanyi was able, assuming a dissociation of the components of the electrolytic gas reaction into atoms, to make plausible the required decrease of 30 kilocals. in the activation energy of water formation. It is clear that energy effects of the order of magnitude of chemical binding energies must be involved. Schwab and Pietsch [318] were able, on the same basis, to interpret the order of magnitude of the activation energy of the heterogeneous decomposition of methane, lower by 55 kilocals. than that of the homogeneous reaction. Taylor [280] analyzed, analogously, the decomposition of hydrogen iodide on platinum. A direct experimental support for the rôle of free atoms as intermediate steps in reactions can perhaps be found in experiments of Kistiakowsky,[319, 266] who measured the ionizing potentials of gases adsorbed on metals and found values attributable to gas atoms.

Quantum Mechanics of Activated Adsorption: Recently, these ideas have obtained a more exact interpretation by reason of their association with the quantum mechanical concepts of the homopolar chemical bond. The older Lewis-Langmuir-Kossel concept of this bond permitted a formal interpretation of its stoichiometric character and certain conclusions concerning its selectivity, in that each valence bond was ascribed to a shared electron pair, for example, in orbits around both atoms. It was, however, quite an open question what the nature of the attractive force was which could be set up as a result of such electron pairing. Wave mechanics ascribes the older orbital motion of the electrons to a wave process and the formation of an electron pair implies that the corresponding wave motions of the two atoms engage in resonance with one another. There results a force, which is described by the formulae of wave mechanics, and which can produce attraction or repulsion but which is different in nature from the Coulomb forces of ion attraction and from dipole attraction and also is more important in magnitude than these.

[318] G.-M. Schwab and E. Pietsch, *Z. physik. Chem.*, **121**, 189 (1926); **126**, 473 (1927); *Z. Elektrochem.*, **32**, 430 (1926).

[319] G. Kistiakowsky, *J. Phys. Chem.*, **30**, 1356 (1926).

With this theory it is possible not only to understand homopolar valence, at least qualitatively, but also, and this especially interests us here, to interpret activation energy and discuss its changes. London,[320] who has played an important part in the development of these concepts, has carried this out to what is known as the first approximation.

The energy of interaction between two atoms at a distance a consists of two parts, the coulombic term $A(a)$ and the resonance effect $\alpha(a)$. It is therefore expressible by

$$W(a) = A(a) \pm \alpha(a).$$

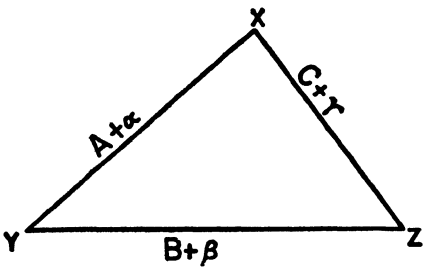


FIG. 31a. Binding Energies of Three-Atom System.

The positive sign in α signifies an attraction, the negative a repulsion by resonance. Of the two possibilities, only the first is realized with hydrogen in a stable molecule. If now, we consider three atoms X, Y, and Z, at distances a, b, and c, from one another as shown in the accompanying diagram, the interaction between two atoms has the following values when the third atom is infinitely far removed

$$\text{Between } X \text{ and } Y : W(a) = A(a) \pm \alpha(a)$$
$$\text{Between } X \text{ and } Z : W(b) = B(b) \pm \beta(b)$$
$$\text{Between } Y \text{ and } Z : W(c) = C(c) \pm \gamma(c).$$

These interactions will be changed as the three atoms approach one another in a characteristic but not additive fashion, that is to say, the parallelogram of forces is not applicable to these forces which are dependent on each other. For the total interaction energy of the system the following values are possible

$$W_1 = A + B + C - \alpha - \beta - \gamma$$
$$W_2 = A + B + C + \alpha + \beta + \gamma$$
$$W_3 = A + B + C$$
$$W_4 = A + B + C \pm \sqrt{\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha}.$$

The case of repulsion, W_1, does not lead to molecule formation. The case of the simultaneous attraction of all three atoms, W_2, is forbidden by the Pauli-principle; of the three equivalently bound valence electrons, two must also have parallel spins (magnetic moment) and the Pauli-principle states that two identical electrons of equal binding and equal spins cannot be present in one molecule. This principle contains therefore the chemical

[320] F. London, *Z. Elektrochem.*, **35**, 552 (1929).

concept of definite valence values; XY would be a saturated molecule not capable of binding Z; compare in this respect the non-existence of H_3.

The behavior of the three atoms of our example is therefore described by W_3 and W_4, and actually by the state possessing the lower energy. The square root factor in W_4 represents the resonance energy. We can approximately describe the variation of the energy on the approach of an atom Z to a molecule XY by inserting the functions α, β, and γ. It is found that the approach of the atom results first in the bond between X and Y being weakened and in the repulsion of Z. If the reaction $XY + Z = X + YZ$ is exothermic there finally results, on nearer approach, an attraction of Z and a repulsion of X. The energy, therefore, passes through a potential barrier and the system must possess this maximum energy before it can approach the distances at which attraction occurs. This barrier plays the part of an activation energy.

The development of London's concept was initiated by Eyring and Polanyi [320a] on the basis of the equation for W_4 which expresses the total energy of a system of three atoms in terms of the bond energies between atom pairs, $A + \alpha$, $B + \beta$ and $C + \gamma$. These energies at various atom distances are obtainable from spectroscopic data and, as was suggested by Eyring, most conveniently by constructing potential energy curves for diatomic molecules with the aid of the empirical equation, due to Morse,[320b] which expresses the potential energy by means of the equation,

$$P = D'(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}).$$

Here D' is the heat of dissociation of the molecule plus the zero point energy ($= \frac{1}{2} h\nu$), r is the nuclear distance, r_0 the equilibrium nuclear distance of the molecule, a is a constant and equal to $0.1227\nu_0 (M/D')^{\frac{1}{2}}$ where M is the reduced mass and ν_0 is the classical frequency of vibration. In this equation, ν_0 is expressed in wave numbers per cm., r and r_0 in Ångström 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, $D + \delta$. 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 [320c] for the hydrogen molecule, the coulombic part in this case is approximately ten per cent of the total.

[320a] H. Eyring and M. Polanyi, *Z. physik. Chem.*, B **12**, 279 (1931).
[320b] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).
[320c] Y. Suguira, *Z. Physik*, **45**, 484 (1927).

Eyring and Polanyi were, therefore, in a position to apply the London equation to the three atom problem

$$H_{2para} + H = H_{2ortho} + H$$

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

$$W_4 = A + B + C \pm (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha)^{1/2}$$

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

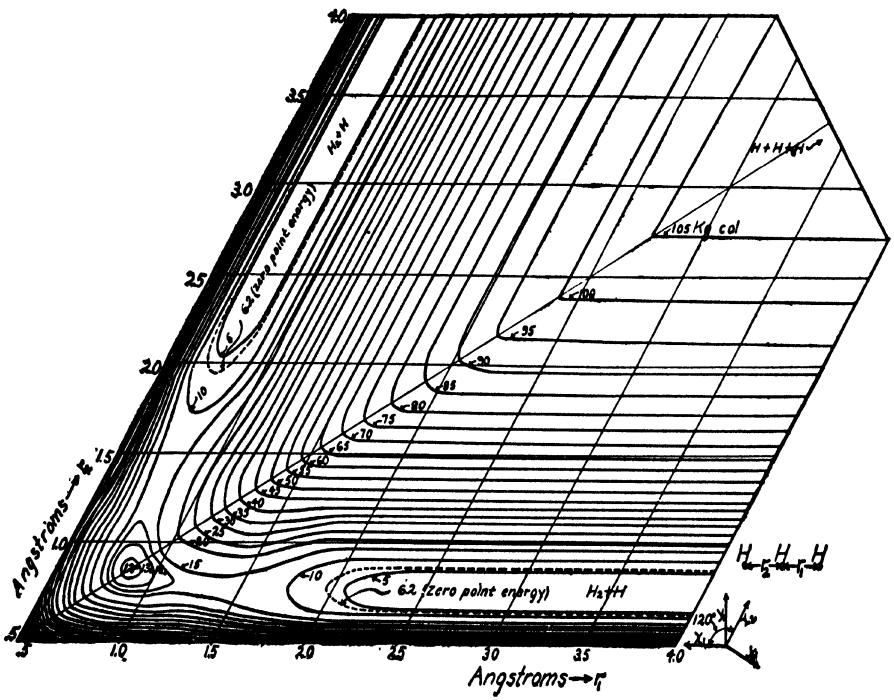


FIG. 31*b*. Potential Energy Diagram for the System $H_2 + H$.

and Polanyi, 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 r_1 and r_2 as ordinates and abscissae could be recorded in the form of contour lines of equal energies, representative of a potential energy surface. As shown by the diagram, Fig. 31*b*, the surface resembles two long, deep-val-

leys stretching to infinity parallel to the axes. As one travels up the valley towards the origin one climbs slowly to a height of 13 kilocals. which is the activation energy of the reaction through a shallow basin 1.6 kilocals. deep to a gap in the basin rim again 13 kilocals. high and descends slowly to the second valley. The activation energy of the process, is the least energy, 13 kilocals. which will enable the system to pass from the conditions represented by the extreme end of one valley to that of the second. It is of interest to record that actual experimental determinations of the activation energy of the process in question as determined first by Farkas [320d] and later by Geib and Harteck [320e] give an observed activation energy of 7.2 kilocals. This must be regarded as a very satisfactory agreement between theoretical calculation and experiment. More recently, in an extended application of this equation to this reaction, which included consideration of all the various possible modes of approach of the reacting species, Pelzer and Wigner [320f] were able not only to deduce the activation energy but also the actual rate of reaction.

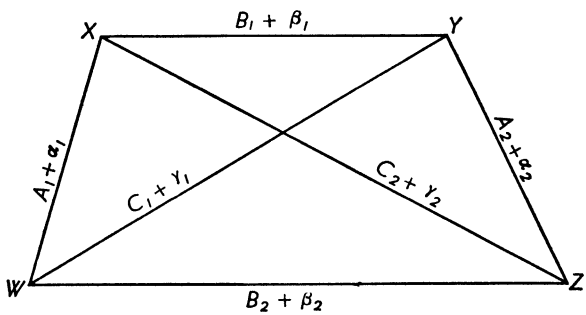


FIG. 31c. Binding Energies of a Four-Atom System.

Eyring [320g] next applied this method of calculation of activation energy to four univalent atom systems, the potential energy equation for which is

$$P = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + [\tfrac{1}{2}(\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2]^{\frac{1}{2}}$$

in which the significance of A, B, C, etc., are apparent from the accompanying diagram, Fig. 31c. In these cases, the most favorable approach of the two molecules is in a plane. Eyring applied this equation to six reactions

[320d] A. Farkas, *Z. physik. Chem.*, B 10, 419 (1930).
[320e] K. H. Gieb and P. Harteck, *ibid.*, Bodenstein Festband, 849 (1931).
[320f] H. Pelzer and E. Wigner, *Z. physik. Chem.*, B 15, 445 (1932).
[320g] H. Eyring, *J. Am. Chem. Soc.*, 53, 2537 (1931).

of the type

$$AB + CD = AC + BD$$

including the reactions of hydrogen and the halogens and a possible bimolecular interconversion of para-ortho-hydrogen. He found, in agreement with experiment, that reactions of halogens with hydrogen will, with the exception of iodine, proceed more readily by a mechanism involving a three atom interaction of one atom and one molecule, for example,

$$\begin{aligned} Cl + H_2 &= HCl + H \\ H + Cl_2 &= HCl + Cl \end{aligned}$$

rather than by the straight bimolecular mechanism

$$H_2 + Cl_2 = 2HCl.$$

The same is true of the para-hydrogen conversion. A more detailed examination of the hydrogen-chlorine combination including the influence of water vapor and the possibility of such five atom reactions as

$$H + H_2 + Cl_2 = 2HCl + H$$

has shown [320h] that all alternative mechanisms than the atom-molecule chain involve larger activation energies. This latter paper treats also the general problem of five electron reactions in quantum mechanics. These studies have been followed by numerous researches by Eyring and his coworkers on homogeneous reaction kinetics involving three or more atoms (1932–1936).

The extension of this method of attack on problems of reaction kinetics to the reactions occurring at surfaces has been initiated by Sherman and Eyring.[320k] They applied the methods of Eyring and Polanyi to the calculation of activation energies of adsorption at surfaces, and examined the interaction of a hydrogen molecule with a carbon surface. The process may be visualized as the approach of a hydrogen molecule to two particular carbon atoms in the surface and the formation of two C—H bonds. The problem is a variant of the four atom problem already discussed in that by their attachment to a solid surface the distance of the two carbon atoms is fixed and unchanging. The adsorption process replaces a single bond of 101.5 kilocals. between the hydrogen atoms and a weaker one between the carbon atoms by two C—H bonds whose combined strength does not exceed by more than a few kilocalories (the heat of adsorption) the strength of the two bonds broken.

[320h] G. E. Kimball and H. Eyring, *J. Am. Chem. Soc.*, **54**, 3876 (1932).
[320k] A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

Sherman and Eyring found that the activation energy of the process was very sensitive to the carbon-carbon distance. The two curves in the diagram Fig. 31*d* are obtained upon two different assumptions with respect to the nature of the carbon-carbon bond broken. The curves show that, in each case, the reaction proceeds with the lowest activation energy for carbon atoms at a distance of 3.6 Å. This sensitivity of activated adsorption to

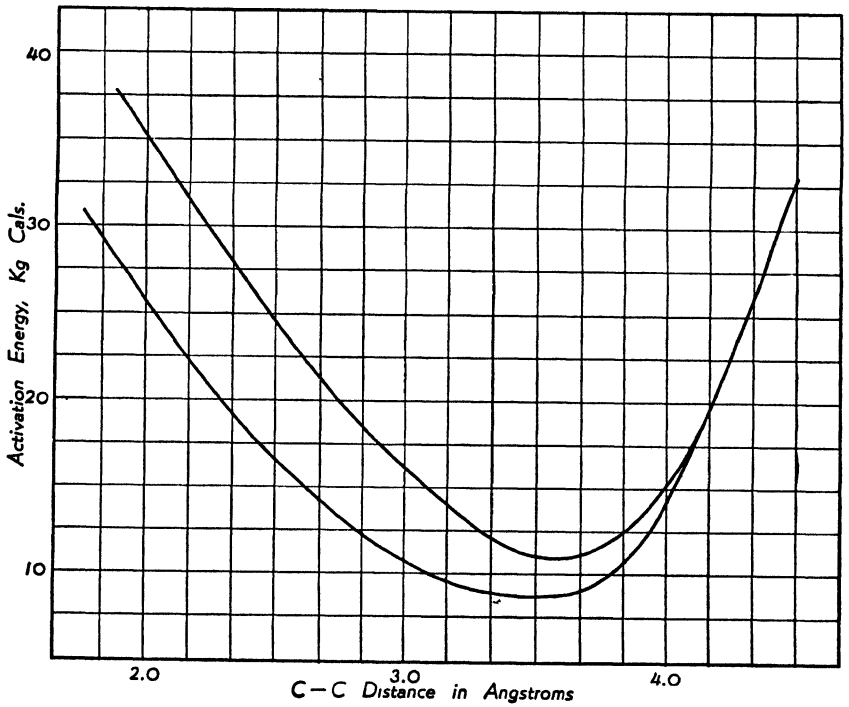


FIG. 31*d*. Dependence of Activation Energy of Adsorption of H_2 on Charcoal as a Function of the C—C Distance in the Surface.

surface distance is obviously a matter of extreme importance in the technique of catalyst preparation.[320i] The preparation of an active catalyst obviously will involve the preparation of surfaces on which the processes of activated adsorption will occur at as low temperatures as possible. Some indication of the effective securing of such results with the aid of mixed oxide preparations has already been indicated in the previous sections on activated adsorption (page 206).

[320i] As to the importance of atom-atom distance in catalytic agents see the recent papers of J. Eckell, *Z. Elektrochem.*, **39**, 423, 433, 807, 855 (1933).

An examination of the contour maps from which the curves of Fig. 31*d* were constructed reveals that the path of the hydrogen as it approaches the carbon atoms in the surface is of the kind schematically represented in Fig. 31*e*. It is interesting to note that the hydrogen molecule practically reaches the carbon surface before expanding appreciably.

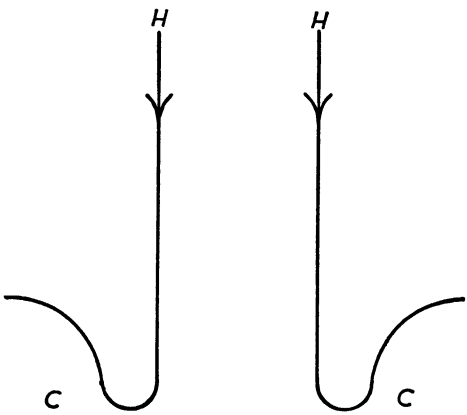


FIG. 31*e*. Path Followed by H_2 when Becoming Adsorbed on Charcoal.

The actual magnitudes of the activation energies calculated in the manner described may deviate markedly from actual measurements. It should be pointed out, however, that all these calculations are sensitive in absolute magnitude to the percentage distribution of the total energy of a bond between the coulombic and interchange energies. By changing the percentage of coulombic binding from 10 to 14 per cent for both C−C and C−H bonds Sherman and Eyring show that the minimum activation energy is reduced from 8.8 to 5.6 kilocals. They also point out that, with the higher coulombic ratio, calculations made by them for the activation energy of hydrogenation of ethylene agree with the value found experimentally by Pease [320m] for this reaction.

Sherman and Eyring considered the alternative possibility of the ortho-para conversion involving the collision of a molecule from the gas phase with an adsorbed hydrogen molecule. This involves the solution of the six electron problem, which they achieved. The results show, however, that this method of conversion as well as the homogeneous reaction of two hydrogen molecules in the neighborhood of two surface carbon atoms are both processes of one order of magnitude higher activation energy than that involved in exchange of atoms from two adjacently adsorbed hydrogen molecules. There are theoretical reasons for excluding a conversion resulting from the dissociation of a single molecule of hydrogen by surface carbon atoms followed by recombination. It, therefore, appears that the surface reaction is identical with the homogeneous reaction and expressed by the equation

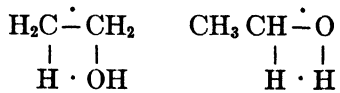
$$H + H_{2para} = H_{2ortho} + H.$$

[320m] R. N. Pease, *J. Am. Chem. Soc.*, 53, 2537 (1931).

One further point of interest may be emphasized in surface processes which these quantum mechanical studies indicate as involving activated adsorption. At sufficiently low temperatures, of the sequence of processes involved in the para-hydrogen conversion (*a*) activated adsorption, (*b*) reaction of adjacently adsorbed species and (*c*) desorption, it is apparent that the rate of process (*c*) will be the determining factor. Now, as was pointed out by Taylor,[321] the activation energy of desorption E_d is composite of the activation energy of adsorption E_a and the heat of adsorption, Q; $E_d = E_a + Q$. Under conditions where desorption is the controlling factor, it is evident that there are two demands on an efficient catalyst namely that both E_a and Q shall be as small as possible.

Incomplete Dissociation on Adsorption: In many cases, the adsorption energy of the active state or, in other words, the binding energy of the molecular fragments or radicals with the contact mass, cannot yield the total dissociation energy of the reactants. It is then necessary to supply additional activation, the substrate is not completely split up, has still a residue of internal attraction, is expanded. The concept herein outlined, which originally only covered complete dissociation, passes continuously over into the concept of a deformation of the adsorbate, which Raschig [322] put forward quite generally as long ago as 1906, and Boeseken [323] and Bodenstein [324] later advocated on the basis of organic-chemical and physicochemical considerations respectively.

Balandin's Multiplet Hypothesis: The discussion of organic chemical material concerning catalytic hydrogenation and dehydrogenation, from a point of view very close to that of Boeseken just mentioned, has proved very fruitful in the hands of Balandin.[325, 326] To the postulate that the binding between atoms is broken, if they are attracted by two different catalyst atoms, Balandin adds another postulate that, between atoms bound to the same catalyst atom, a bond is closed. For example, the dehydrogenation and dehydration of alcohols which occur simultaneously on various oxides may be interpreted by the following scheme



[321] H. S. Taylor, *Chem. Rev.*, **9**, 34 (1931).
[322] F. Raschig, *Z. angew. Chem.*, **19**, 1748 (1906).
[323] J. Boeseken, *Rec. Trav. chim. Pays-Bas.*, **45**, 458 (1926).
[324] M. Bodenstein, *Lieb. Ann.*, **440**, 177 (1924).
[325] A. A. Balandin, *Z. physik. Chem.*, B **2**, 289 (1929).
[326] A. A. Balandin, *ibid.*, B **3**, 167 (1929).

If the dots represent the adsorbing catalyst atoms it is clear that, on the basis of the two postulates, ethylene and water will be formed in the first case and hydrogen and aldehyde in the second. Catalysis arises, according to this view, through the geometrically determined action of various catalyst centers; hence the name given by Balandin to his hypothesis: the multiplet-hypothesis. In its essential point, similar views had previously been put forward by Burk [327] under the title " multiple adsorption."

Balandin now goes further and discusses the dehydrogenation of hydroaromatic rings, in the same manner, in that he arranges the six membered ring on the octahedral face of a face-centered cubic metal lattice, this face having a regular triangular atomic lattice as shown in Fig. 32. The three platinum atoms 1, 2, 3 extend the distances between the carbon atoms which lie between them, while the three platinum atoms, 4, 5, 6 attract pairs of neighboring hydrogen atoms and cause them to combine. This sextet model leads to the conclusion, then accepted, that only face-centered cubic metals dehydrogenate, and that, further, their lattice constants must lie between two limits. Actually, hydrogenation is possible with metals whose lattice constants lie between 1.397 Å. (Pd) and 1.237 Å. (Ni), whilst metals with constants lying only slightly outside these limits (Sn = 1.40 Å.) are inactive. However, it remains to be seen whether these specialized geometrical concepts have not been driven too far.[327a]

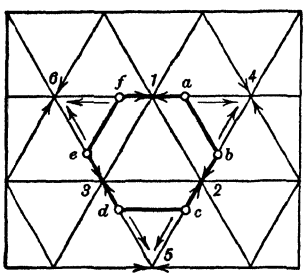


FIG. 32. Dehydrogenation of a Six-Membered Ring (Balandin).

For processes at a single carbon-carbon bond, the concept seems to be confirmed, as indicated by the fact that the activation energy is de-

TABLE XXXIV — ACTIVATION ENERGY IN KILOCALS. PER MOL

Dehydrogenation of	Piperidine	Cyclohexane	Decalin
On Palladium	16.3	15.3	—
On Nickel	—	9.7	10
On Platinum	19.9	18.0	18.9

[327] R. E. Burk, *J. Phys. Chem.*, **30**, 1134 (1926).

[327a] In this connection, attention is directed to a paper by W. A. Lazier and J. V. Vaughen, *J. Am. Chem. Soc.*, **54**, 3080 (1932) in which they discuss Balandin's theory on the basis of dehydrogenation results obtained with oxide catalysts not possessing the geometry suggested. Tr.

pendent only on the catalyst, not on the substrate. The previous table [328] indicates this.

Confirmation that activation is obtained through the heat of adsorption of the activated state results quite definitely from the study of decomposition reactions accompanying hydrogenation of the general types:

$$\equiv C-X + H_2 = \equiv CH + HX-$$
$$-Y-Z + H_2 = -YH + HZ-$$

By investigating the fragments from the hydrogenation of compounds which contain several such divisible bonds in the one molecule, the order of breaking such bonds kinetically can be deduced. The discussion of a comprehensive set of data taken from Sabatier's book on Catalysis [329] leads Balandin [326] to the conclusion that this order is actually a definite one, that, indeed, the bonds break with increasing velocity in the following order:

$$C-C;\ C-N-;\ =N-N=;\ C-O-;\ =N-O-;\ C-Br;\ C-Cl.$$

The fact that the stability, towards hydrogenation, of atoms bonded to carbon shows the same stepwise variation that the same atoms show when bound to nitrogen leads to the conclusion that there is some additive influence of the atoms bound. Balandin succeeds in showing that the binding energy of the bond to be broken less the heats of adsorption of the fragments (estimated from the heats of formation of nickel halides, oxide, nitride and carbide) falls in the same order. This calculated energy is actually the theoretical activation energy calculated according to the principles we have already laid down. It is thus proved that the catalytic activation energy can really be satisfactorily indicated by the components introduced.

At this point a remarkable additivity of activation energies may be mentioned, discovered by Dohse,[329a] for the dehydration of alcohols at bauxite surfaces. The extrapolated 'base activation energy' of 36.5 kilocals. for all carbinols is lowered by substitution. A methyl, methylene, or methin substitution in the α-position lowers it by 5.5 kilocals., in the β-position by 2–5 kilocals., and in the γ-position by 0.5 kilocals. The activation energies of normal and branched alcohols up to tertiary amyl alcohol can thus be well reproduced. The lowering produced by substitution, which diminishes approximately with the cube of the distance, must be interpreted as the influence of the substituent on the bond to be broken.

[328] N. D. Zelinsky and A. Balandin, *Z. physik. Chem.*, **126**, 267 (1927).

[329] Catalysis in Organic Chemistry, Sabatier-Reid, D. Van Nostrand and Company, New York, 1922.

[329a] Dohse, *Z. physik. Chem.*, Bodenstein Festband, 533 (1931).

Catalytic Activity and the Periodic Classification: A more important point of view of quite another kind must now be mentioned. It is apparent that the metals, which are capable of displaying varied catalytic activity, are congregated in a fairly limited region in the last group of the periodic system and comprise, for example, all the elements of the platinum and iron groups. These are predominantly metals of variable valence,[330] with poorly defined electron sub-groups. The metals of the eighth group, especially, possess incomplete shells of electrons. Also, in compounds, colored substances which contain loosely bound valence electrons seem to be preferred.[331, 332]

Although the division of electrons into sub-groups really concerns the isolated atoms, we may, however, assume with V. M. Goldschmidt [333] and A. S. Russell [334] that the corresponding lattices have an "M-defect" or "electron hunger" or that they have a tendency, through single electrons in inner shells, which are not yet trapped in the "electron gas" of the solid metals, to enter into resonance with adsorbed atoms, that is to say, to bind these latter in a homopolar manner. This remarkable selection rule for catalysts is thus related to the requirement that the activation of homopolar adsorption presupposes; the lattice parameter previously discussed (page 252) would not then be the sole parameter for catalytic activity.

The State of Adsorbed Hydrogen: Hydrogen merits special consideration with respect to its state on the surface of a catalyst. We have seen already, that measurements of the ionization potential of adsorbed hydrogen (page 242) indicated that it was present in the atomic form. We saw further (page 191) that the method of electron interference had shown the bonding of hydrogen at points in a two-dimensional surface lattice. Both are in agreement with the requirement that it be chemically bound to surface atoms, even if such a binding does not exclude "hopping" from one atom to another, a "melting" therefore of the adsorbate crystal. (See, for example, Germer, page 192.)

On the other hand, there are serious grounds for believing that hydrogen is present in metals in the form of ions. We have already pointed out (page 242) that Bennewitz and Günther [317] have made this probable and O. Schmidt [316] has drawn conclusions from this concerning the rôle of ions

[330] B. K. Mereschkowsky, *Bull. Soc. Chim. biol. Paris*, **39**, 41 (1926).
[331] S. Roginsky and E. Schultz, *Z. physik. Chem.*, A **138**, 21 (1928).
[332] G.-M. Schwab and H. Schultes, *ibid.*, B **9**, 265 (1930).
[333] V. M. Goldschmidt, *Z. techn. Physik.*, **8**, 251 (1927).
[334] A. S. Russell, *Nature*, **117**, 47 (1926).

in catalytic hydrogenation. New, elegant investigations of Coehn [315,334a] have provided a direct proof of the presence of protons, in palladium especially. By passage of the current through the metal the dissolved hydrogen migrates electrolytically towards the cathode, which migration, by application of a potential, is measurable by the change of the electrochemical hydrogen potential in the wire, by migration of the region of high resistance and finally by the migration of a region which, with air, yields hydrogen peroxide, a product which can be located photographically.

There seems therefore to be a contradiction between two sets of experimental results. It is, however, possible that this is only apparent. If the hydrogen is dissolved in the metal in the form of protons and electrons, the protons, as compared with their medium must appear to be positive ions. On the other hand, they are surrounded by such an excess of the electrons of the metal, that, from an external point of view, for example, due to bombardment with electrons (Kistiakowsky), or in surface reactions (Polanyi), they must behave as protons bound to electrons and, therefore, similarly to atoms. The problem as to whether the charge or the binding of the hydrogen signifies its activation may well, therefore, be two aspects of the same thing.

Only one reaction of hydrogen is exceptional, the conversion of ortho- to para-hydrogen on charcoal at low temperatures.[334b] We have already seen that atomic adsorption, taking place on metals at high temperature produces immediate transformation governed by the velocity of adsorption and desorption. On charcoal at temperatures under 100° K., adsorption occurs without change and the hydrogen only slowly goes over into the equilibrium mixture, unimolecularly in the adsorption layer. In this case the conversion does not depend upon an activation or dissociation but on an influence on the isolated adsorbed hydrogen molecules exercised by the paramagnetism of single unsaturated surface carbon atoms. The rapid conversion of ortho- to para-hydrogen at such low temperatures as observed on chromic oxide gel and various paramagnetic oxides [334c] confirms this view. These surface reactions correspond to the homogeneous conversions due to paramagnetic gases and paramagnetic ions in solution,[334d] and to the surface conversion of ortho- to para-hydrogen at solid oxygen sur-

[334a] See also, D. P. Smith and F. H. Martin, *J. Am. Chem. Soc.*, **38**, 2577 (1916); E. A. Harding and D. P. Smith, *ibid.*, **40**, 1508 (1918); **41**, 1892, 1897 (1919); Smith, *Trans. Am. Electrochem. Soc.*, **34**, 177 (1918); *Proc. Nat. Acad. Sci.*, **7**, 28 (1921).

[334b] K. W. Rummel, *Z. physik. Chem.*, A **167**, 221 (1933).

[334c] H. S. Taylor and H. Diamond, *J. Am. Chem. Soc.*, **57**, 1251 (1935).

[334d] Farkas and Sachsse, *Z. physik. Chem.*, B **23**, 1 (1933).

faces.[334e] In this case, forces of adsorption of the magnitude of heats of vaporization are involved.

Intermediate Compounds

It has already been pointed out (page 202) that the assumption of adsorption as the intermediate stage of catalysis is not different in nature from the occurrence of chemical intermediate compounds. Now that we have learned more precisely the chemical character of the adsorption which is effective, this identity becomes even clearer. Whether a non-stoichiometric intermediate compound can be realized and studied depends upon whether, under the conditions of the catalysis, it possesses the necessary lifetime, or whether the adsorption covers a sufficiently large area of surface. In any case, it has been possible in a large number of cases to study the substrate in its bound condition.

Rupp[259] believed that he was able to furnish a proof for the rôle of adsorbed hydrogen on iron and nickel in ammonia synthesis. The surface lattice of adsorbed hydrogen as revealed by electron interference (see pages 191 and 193), disappears when nitrogen is allowed access to the catalyst, while nitrogen in contact with the gas-free catalyst does not change it in this way. The formation of ammonia, and that the ammonia formed is not adsorbed in the form of a lattice, were deductions to be drawn from these observations. In the meantime, the experiments have been objected to and, as we shall see, the results are doubtful because it has been shown that nitrogen and not hydrogen must first be activated.

The binding of hydrogen to iron, the most important ammonia catalyst, was directly investigated by Frankenburger and Mayrhofer[335] in still another manner. They evaporated an iron wire in hydrogen and found that hydrogen was bound thereby to the iron. Recrystallization of the iron deposited on the vessel wall decreased the amount of hydrogen taken up, so that it must be concluded that a surface adsorption had occurred. How this recrystallization could be prevented is a point of especial interest in another connection, that of mixed catalysts. In any case these experiments showed that valence forces exist between hydrogen and iron atoms in special positions.

Mittasch and Frankenburger[336] have examined the same problem in the case of nitrogen. At first, and under the same experimental conditions, nitrogen was not fixed by the iron but, according to private advices, a

[334e] Cremer, *Z. physik. Chem.*, B **21**, 459 (1933).
[335] W. Frankenburger and K. Mayrhofer, *Z. Elektrochem.*, **35**, 590 (1929).
[336] A. Mittasch and W. Frankenburger, *Z. physik. Chem.*, A **139**, 386 (1928).

binding of nitrogen to iron atoms has now been established.[336a] The recent data of Emmett and Brunauer [336b] indicate that in technical ammonia catalysts it is this binding of nitrogen to the catalyst surface which determines the rate of ammonia synthesis.

On tungsten, Messner and Frankenburger [336c] later demonstrated this relation to catalysis. At moderate temperatures, ammonia decomposes and gives surface imides and finally nitrides. On the other hand, the nitride can be obtained from tungsten and nitrogen in an exothermic reaction and it is then possible to decompose it with hydrogen. The nitride obtained with nitrogen breaks down into tungsten and nitrogen at the same temperature at which ammonia is completely decomposed catalytically. The same nitride is, therefore, an intermediate for formation and decomposition.

In the decomposition of ammonia on iron, Mittasch, Kuss and Emmert [337] succeeded in showing the rôle of a definite nitride of iron as an intermediate stage, in that they have measured its rate of decomposition and shown it to be equal in velocity to that of the ammonia decomposition.

All these nitride and imide decomposition reactions [337a] determine reaction rate at lower temperatures and thus permit an analysis of the surface phenomena in terms of chemical compounds. At still higher temperatures, the slowest of all the processes will be the first attack on the adsorbed ammonia molecule. There results, therefore, the fundamental picture of a unimolecular reaction of the adsorbate set forth on page 219. For a more extended discussion of these points a number of references are available.[337b]

Another case in which the reaction has been proved to occur through an intermediate compound may be mentioned: the decomposition of dissolved

[336a] Our knowledge of activated adsorption indicates that, in the case of nitrogen, adsorption by iron would require a marked activation energy and would first be noted in a higher temperature range than is necessary with hydrogen. See H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 595 (1931); A. F. Benton, *Trans. Faraday Soc.*, **28**, 202 (1932). W. Frankenburger, and Hodler, *ibid.*, **28**, 229 (1932).

[336b] Emmett and Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934).

[336c] Messner and Frankenburger, *Z. physik. Chem.*, Bodenstein Festband, 593 (1931).

[337] A. Mittasch, E. Kuss and O. Emmert, *Z. Elektrochem.*, **34**, 829 (1928).

[337a] See E. Winter, *Z. physik. Chem.*, B **13**, 401 (1931).

[337b] Schwab, Rudolph and Schneller, Gmelins Handbuch d. Anorg. Chem., System number 4, Nitrogen, Ammonia, Formation and Decomposition. Frankenburger, *Z. Elektrochem.*, **39**, 45, 97, 269 (1933). C. Kröger, *Z. anorg. Chem.*, **194**, 73 (1930); **205**, 369 (1932); **206**, 289 (1932) *Z. Elektrochem.*, **39**, 670 (1933). Emmett and Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934), Jungers and Taylor, *J. Am. Chem. Soc.*, **57**, 660 (1935).

hydrogen peroxide on silver, studied by Wiegel.[338] It was shown that colloidal silver is soluble in aqueous hydrogen peroxide to an extent governed by the solubility product,

$$(Ag^{\cdot})\ (OOH') = \text{const.},$$

alkali lowering the solubility. As soon as the solubility product concentration is exceeded, AgOOH is produced, adsorbed on silver particles; that is to say, a surface of AgOOH forms as an intermediate stage and reacts with hydrogen peroxide thus:

$$\begin{matrix} Ag-OOH \\ \dot{A}g-OOH \end{matrix} + HOOH = 2H_2O + 2O_2 + \begin{matrix} Ag \\ \dot{A}g \end{matrix}$$

$$\begin{matrix} \dot{A}g-OOH \\ \dot{A}g-OOH \end{matrix} + HOOH = 2H_2O + 2O_2 + \begin{matrix} \dot{A}g \\ \dot{A}g. \end{matrix}$$

The silver formed remains behind on the catalyst. That this is the correct interpretation is apparent from the fact that the limiting concentration of the catalysis is given by the solubility product, but, above all, because the silver particles increase in size during the catalysis, changing their color to blue.

The contact sulphuric acid reactions at oxide surfaces, in which the adsorption compounds may be identified as isolable compounds, are very well-known, older examples of intermediate product catalyses. Thus, with Neumann,[279] in a somewhat simplified and abbreviated form, we may formulate the Fe_2O_3 catalysis thus:

$$\begin{aligned} SO_2 + 3Fe_2O_3 &= 2Fe\,O_4 + SO_3 \\ 2Fe_3O_4 + 2SO_2 + O_2 &= 2Fe_2O_3 + 2FeSO_4 \\ 2FeSO_4 + \tfrac{1}{2}O_2 &= Fe_2O_3 + 2SO_3 \\ \hline 3SO_2 + 1.5O_2 &= 3SO_3 \end{aligned}$$

Ferrous sulphate as an intermediate step is directly established. With titanium oxide we have:

$$\begin{aligned} 2TiO_2 + SO_2 &= Ti_2O_3 + SO_3 \\ Ti_2O_3 + 1.5O_2 + 3SO_2 &= Ti_2(SO_4)_3 \\ Ti_2(SO_4)_3 + \tfrac{1}{2}O_2 &= 2TiO_2 + 3SO_3 \\ \hline 4SO_2 + 2O_2 &= 4SO_3 \end{aligned}$$

In this case, also, the sulphate, $Ti_2(SO_4)_3$, has been shown to exist. It is illuminating that these catalyses first begin at temperatures at which the SO_3-dissociation pressure of the sulphate in the third equation reaches one

[338] E. Wiegel, *Z. physik. Chem.*, A **143**, 881 (1929).

atmosphere. Otherwise the SO_3, remaining "adsorbed," acts as a retardant.

Other Mechanisms of Contact Catalysis

In the following paragraphs we shall exclude those cases of catalysis which depend on a lowering of the activation energy. Besides these, there naturally exist other possibilities that may influence the constant Z, in the equation on page 240, due to presence of a solid surface. The increased velocity indicates catalysis, although it has been shown that the greatest increases observed do not occur in this way (pages 240 et seq.).

In the first place, the probability of reaction following a collision can be increased, without change of the necessary energy, through the catalyst insuring that the molecules collide on their reactive ends. Such an effect is certainly to be expected, since adsorption exercises a directive action. This is easy to understand, since a homopolar force of adsorption can only exert itself at a definite position in the molecule. Orientation due to adsorption has been demonstrated, for example, through the fact that all the alcohols show the same activation energies for dehydrogenation [339] and for dehydration.[303] There are also many direct X-ray and other observations of this fact.

Such an orientation can accelerate the reaction by increasing the number of favorable collisions; it can, however, also inhibit, in that it may turn the reactive portions of the molecule towards the catalyst and so make them inaccessible. Kruyt [340] has observed examples of both types of orientation with organic molecules at charcoal surfaces. In no case, however, did the changes in velocity equal those obtained by activation due to the contact mass.

In the second place, considerable accelerations through orientation are possible if the slowness of reaction is due, not to a lack of activation energy but to a lack of nuclei for a new phase which is being formed. In this case, directed adsorption on a foreign substance can operate to establish nuclei, thus destroy the supersaturation and so permit the reaction. We shall learn more of this mechanism later with reactions in which solid phases result (see page 327). It can, however, accelerate a reaction of one set of gases to form another, if such a reaction occurs through such a solid phase-forming reaction as an intermediate stage. For example, Okayama [341]

[339] W. G. Palmer and F. H. Constable, *Proc. Roy. Soc.*, A **107**, 255 (1925); F. H. Constable, *ibid.*, A **113**, 254 (1927).

[340] H. R. Kruyt, *Z. Elektrochem.*, **35**, 539 (1929).

[341] J. Okayama, *Z. Elektrochem.*, **34**, 294 (1928).

discusses the combination of hydrogen and oxygen from this standpoint. It probably occurs through the stages

$$(1) \quad 2Cu + O_2 = 2CuO$$
$$(2) \quad 2CuO + 2H_2 = 2Cu + 2H_2O,$$

and the discussion of the equilibrium position shows that at least the first of the two reactions probably does not go in the absence of copper oxide. This is in agreement with the fact that the whole catalysis occurs only at the boundary Cu—CuO (cf. page 232). Nevertheless, a reduction in the activation energy at such a boundary line is one possibility (see page 330).

Another manner, in which a solid surface can accelerate the velocity has already been treated in a fundamental way (page 54 et seq.). It is a question of the third partner in reactions which, owing to the necessity of removing energy produced by the process, are only possible, according to Born and Franck[18] in three body processes. For example, the recombination of hydrogen atoms studied by Bonhoeffer [76] is thus accelerated by surfaces of different kinds. We shall meet many other cases of this kind (page 317) which we have already touched upon in the discussion of chain reactions (page 32).

Haber [342] has pointed out in this connection that possibly the great closeness of molecules in the adsorption layer has especial significance in quantum mechanics in that, at smaller distances, the resonance relations between the molecules may be more intimate. In the surface, perhaps, energy can more easily pass from one molecule to another and, hence, yield energy chains in the surface. This is in addition to a possible catalysis of the individual steps of such energy chains by the overcoming of the repulsion of the molecules, according to the mechanism of activation by adsorption already discussed. Whether, however, chain reactions exist on the surface at all is still questionable and will be discussed separately (page 315 et seq.).

We may content ourselves with the mention only, since experimental proof is lacking and also difficult, of a possibility of catalysis also derived from wave mechanics which brings a quite new factor into the question. According to the wave mechanics a wave assigned to an approaching atom does not need to pass over the energy barrier or wall described on page 245; it may pass through the potential wall rather than over it especially when the wall is thin (in Å. units) and especially when, beyond it, there is a state with similar energy to one in front of it. As Franck expresses it, the wave may prefer to go through a tunnel in the mountain rather than over it. (The process is analogous to the penetration of a totally reflected radiation

[342] F. Haber, *Z. Elektrochem.*, **35**, 533 (1929).

into the uppermost thin layer of the reflecting medium.) In this way, for example, α-particles are assumed to leave the nuclei of radioactive atoms through a high potential wall which otherwise keeps them inside.[342a] This penetration of a potential barrier by "tunneling" is fundamental in all the newer work in nuclear transformations.

Born and Franck [343] have applied this point of view to catalysis. Their discussion leads to the result that, in principle, no activation energy is needed if the molecules remain in contact for such a time that the probability of passage through the tunnel becomes marked. An approximate calculation of the reaction $N_2 + 2H_2 = N_2H_4$, as a model of the synthetic ammonia process, yields the result that the change can certainly be expected, without activation, if the molecules remain near to one another for the space of one second. The rôle of the adsorbent would on this view be simply to ensure this long time of contact by adsorption.

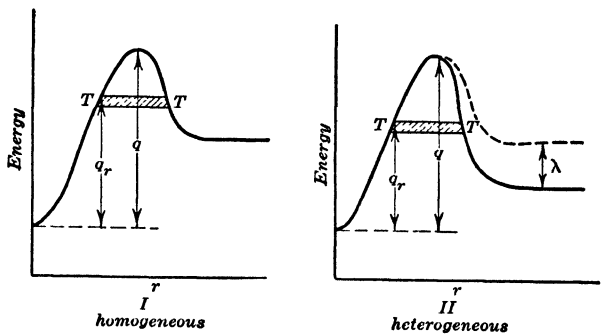


FIG. 33. Lowering of the Necessary Portion q_r of the Energy of Activation q Due to a Heat of Adsorption λ of the Reaction Products (Roginsky and Rosenkiewitsch).

From the same basic assumption, Roginsky and Rosenkiewitsch [344] assign to the contact agent still another rôle: If the reaction products have a large heat of adsorption the adsorbed reaction product is a more stable system than that in the gas phase. In this way, the potential wall, instead of having the form shown in section I of Fig. 33 may have that shown in section II. On this account, the height of the tunnel T, of equal length in the two cases, will be lower, and, consequently, the activation energy, q_r, which will be required is also less. We shall return to this research in another connection later (see page 287).

[342a] R. W. Gurney and E. U. Condon, *Phys. Rev.*, **33**, 127 (1929) and G. Gamov, *Z. Physik*, **51**, 204 (1932).

[343] M. Born and J. Franck, Göttingen Nachrichten, II, 77 (1930).

[344] S. Roginsky and L. Rosenkiewitsch, *Z. physik. Chem.*, B **10**, 47 (1930).

Whether these newest theories will attain to importance in the treatment of catalysis, must remain a question at the present time. In several publications of the last few years, especially those dealing with the ortho-para conversion and the separation of hydrogen isotopes and their reactions, this 'tunneling' mechanism has received marked consideration. It is safe to state that, as yet, no conclusive experimental evidence of the existence of such a 'tunneling' of a potential energy barrier has been forthcoming.[344a] Cremer and Polanyi [344b] calculate, for example, that, according to this conception, a tremendous difference should exist between the velocities of hydrogenation with light and heavy hydrogen. They were unable to find such a difference. The hydrogenation of ethylene was regarded as a reaction without activation energy, largely because of its small temperature coefficient, especially in the neighborhood of the temperature-optimum. Schwab and Zorn showed, as we have seen, that the true activation energy reaches the respectably large value of 20 kilocals.

[344a] For such a discussion see C. E. H. Bawn and G. Ogden, *Trans. Faraday Soc.*, **30**, 432 (1934).

[344b] Cremer and Polanyi, *Z. physik. Chem.*, B **19**, 443 (1931).

CHAPTER XIV

SELECTIVE CATALYSIS AND POISONS

EASE of activation due to adsorption has provided us with an explanation of catalytic acceleration in all the usual cases. It does not, however, explain the phenomenon that a given catalyst, under certain circumstances, accelerates a different reaction among various reaction possibilities from that accelerated by some other catalyst. This phenomenon of selective catalysis has therefore contributed largely to our knowledge of the properties of the surface. At the same time, selectivity is of such astonishing importance for applied catalysis that, for this reason alone, it merits special interest.

It is immediately clear that, for processes which reach a stable equilibrium, a selective action of the catalyst on this equilibrium is not possible (cf. page 15). At 1500° C. from ammonia and oxygen, nitrogen and water will always be obtained, since, at this temperature, the most stable state is immediately set up, regardless of the contact agent used for the reaction. On the other hand, at lower temperatures, as will be seen, single partial reactions of the total process are accelerated more markedly than others. Then, either the process remains in a state of metastable equilibrium or it does not reach any equilibrium at all as a consequence of a premature ending of the experimental conditions, for example, in dynamic systems, as a consequence of rapid streaming of the gases. In this latter case, a more or less accidental intermediate stage will be reached. For example, the concentration of nitric oxide, in the system above discussed, depends upon the ratios of the accelerations produced, which are characteristic for each individual catalyst. These relations have been treated especially clearly by Swietoslawsky.[345]

Types of Selectivity: It is advantageous in this connection to distinguish, with Mittasch,[346] two different kinds of selectivity: The selection of the reaction path to be accelerated by the catalyst can be one from a sequence of stepwise or consecutive reactions, as in the example just discussed. Secondly, however, it may be a matter of a selection from a group of parallel,

[345] W. Swietoslawsky, *J. Chim. Phys.*, **22**, 73 (1925).
[346] A. Mittasch, *Ber.*, **59**, 13 (1926).

alternative reactions such as the dehydrogenation and dehydration of alcohols. Such cases are theoretically important. In more complex systems, both types are possible side by side at various catalyst surfaces. Thus Mittasch [346] gives for the synthesis of organic substances from water gas, the so-called methanol process, the following general scheme

$$CO + H_2 \rightarrow CH_2O \xrightarrow{H_2} CH_3OH \begin{cases} \rightarrow \text{Alcohols} \\ \rightarrow \text{Acids} \\ \rightarrow \text{Ethers and Esters} \\ \rightarrow \text{Aldehydes and Ketones} \\ \rightarrow \text{Hydrocarbons} \\ \rightarrow \text{Cyclic Compounds} \end{cases}$$

The catalyst accelerates either the reaction leading to methanol and represses the succeeding reactions, as does zinc oxide, or alternatively it also accelerates one or other of these successive reactions. By mixing catalysts this latter may especially be achieved. An addition to zinc oxide of chromium oxide and also of alkali leads the reaction further in the direction of higher alcohols. Ferric oxide on the other hand leads to methane and higher hydrocarbons (synthol), sulphur holds back this action of iron.[347]

Successive Reactions

The dehydration of alcohol at surfaces of aluminum oxide may be cited as an important example. Ether is, in this case, the intermediate stage, according to the scheme,

$$2C_2H_5OH \xrightarrow{Al_2O_3} (C_2H_5)_2O + H_2O,$$

$$(C_2H_5)_2O \xrightarrow{Al_2O_3} 2C_2H_4 + H_2O$$

The yields of ether and ethylene at different flow velocities or times of contact show this definitely. Such yields are shown in Fig. 34, from measurements by Alvarado.[348] It can be seen quite definitely that, at 300° C., where the ether is not further decomposed, the ethylene yield remains low. At 354° C., however, after times over half an hour, the ether yield markedly diminishes and the yield of ethylene rises correspondingly, indicating that the latter results from the ether.

The same relations obtain in the synthesis of ethylamine from alcohol and ammonia on bauxite studied by Dorrell.[349] The scheme of reaction is

[347] A. Mittasch, *Z. Elektrochem.*, **36**, 569 (1930).
[348] A. M. Alvarado, *J. Am. Chem. Soc.*, **50**, 790 (1928).
[349] G. W. Dorrell, *J. Chem. Soc.*, **127**, 2399 (1925).

as follows:

$$\text{(I)}\quad C_2H_5OH + NH_3 = C_2H_5NH_2 + H_2O$$
$$\text{(II)}\quad C_2H_5NH_2 = C_2H_4 + NH_3.$$

The ethylamine plays the same part here as the ether in the preceding example; it is the intermediate product of a dehydration process. Here also there exists a region in which, at accelerated velocities of flow or smaller times of contact, the yield of ethylamine rises, quite contrary to what one

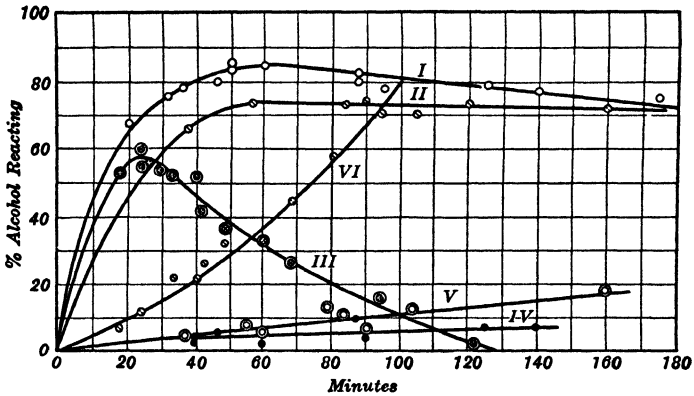


FIG. 34. Ether as an Intermediate Product in the Dehydration of Alcohol on Alumina (Alvarado).

I Ether 269°,	II Ether 300°,	III Ether 354°,
IV Ethylene 269°,	V Ethylene 300°,	VI Ethylene 354°.

would expect with simple reactions. It is probable that this preference for reaction I is due to the strong adsorption of ammonia, which was actually confirmed and which possibly inhibited reaction II by displacement. Kinetic measurements would permit this to be tested.[349a] This idea of " partial poisoning " of one reaction only will interest us again later.

On account of its technical importance, the combustion of ammonia to nitric oxide at contact surfaces has been very thoroughly investigated, especially by Andrussow.[350] With respect to the time of contact at the catalyst the situation is, in this case, exactly as in the preceding, in that the yield of desired product, nitric oxide, falls off with decreasing velocity of

[349a] In this reaction there are additional serious complications resulting from the formation of secondary and tertiary amines which markedly add to the difficulties of such a kinetic study. Tr.

[350] L. Andrussow, *Ber.*, **59**, 458 (1926); **60**, 536, 2005 (1927); *Z. angew. Chem.*, **39**, 321 (1926); **40**, 166 (1927); *Z. anorg. allgem. Chem.*, **166**, 60 (1927). See also W. J. Maliarewsky and N. A. Maliarewskaya, *Z. angew. Chem.*, **38**, 1113 (1925).

flow, since it undergoes decomposition. In addition to this, also, the reactant, ammonia, decomposes partially at slow velocities of flow, in an undesired direction, namely into nitrogen and hydrogen. Similarly the substance preceding the nitric oxide stage may undergo decomposition. A scheme put forward by Bodenstein and Andrussow [351] postulates, in the main, an unstable body, nitroxyl, HNO, which may either decompose like nitric oxide in an undesired direction or may yield nitric oxide, which is the desired path. The scheme is as follows:

The dotted arrows represent spontaneous, homogeneous reactions, the full-line arrows the heterogeneous catalytic reactions. We may note here already a case of selectivity among parallel-occurring reactions.

Formerly, the main objection to this mechanism was that the decomposition of the postulated nitroxyl, HNO, into nitrous oxide and water, although it was to be expected, did not appear to occur. Accordingly, it has been proposed by different people, notably Partington [352] and Raschig,[353] that the intermediate step might be NH. However, v. Nagel [354] has recently succeeded in obtaining nitrous oxide in large amounts at surfaces of manganese dioxide as catalyst. The fact that, under certain extreme conditions, hydroxylamine can also be recovered from the reaction mixture has led Bodenstein [354a] recently to postulate as intermediate stage, in place of HNO, the complex, ONH_3, an isomer of hydroxylamine. This also yields nitric oxide, nitrogen or nitrous oxide and also hydroxylamine according to the operating conditions. The nitric oxide yield shows, besides the obvious lower temperature limit, an upper temperature limit, because, above 600–700° C., the selectivity of the catalyst is lost. At these temperatures, and at any velocity of flow, the undesired reactions are also accelerated to their final equilibrium state.

Alternative Reactions

We turn now to the cases in which the catalyst has to choose between two possible alternative reactions of the same substrate. The phenomena in such cases are in general more understandable kinetically and are,

[351] M. Bodenstein, *Z. angew. Chem.*, **40**, 174 (1927).
[352] J. R. Partington, *Nature*, **117**, 590 (1926).
[353] F. Raschig, *Z. angew. Chem.*, **40**, 1183 (1927).
[354] A. v. Nagel, *Z. Elektrochem.*, **36**, 754 (1930).
[354a] M. Bodenstein, *Helv. Chim. Acta*, **18**, 743 (1935).

therefore, especially valuable for a study of the structure of the active surface. It is a question of alternative reactions such as the following:

$$\text{I} \quad C_2H_5OH = C_2H_4 + H_2O$$
$$\text{II} \quad C_2H_5OH = CH_3CHO + H_2,$$

or

$$\text{I} \quad CH_2 : CHCH_2OH = CH_2 : CHCHO + H_2$$
$$\text{II} \quad CH_2 : CHCH_2OH = CH_3CH_2CHO,$$

or

$$\text{I} \quad HCOOH = H_2 + CO_2$$
$$\text{II} \quad HCOOH = H_2O + CO.$$

These occur side by side at a given surface, or, in the limiting case, the catalyst accelerates one of the two. Thus, according to Sabatier,[329] metals such as active copper give practically exclusively aldehyde from alcohol, whereas aluminum oxide yields only ethylene, and other oxides, especially titania and zinc oxide, accelerate both reactions.

Formic acid decomposes on glass as a first order reaction, in both the above mentioned directions.[355] At 280° C. both velocities are alike but the activation energies are about 12 kilocals. different from each other, being 28 and 16 kilocals. respectively. If, now, it was a question, in both reactions, of the same adsorbed molecule, since the share of λ the heat of adsorption in E_a, the apparent activation energy, would then be the same in the two cases, the result obtained would not be comprehensible without further assumptions, since, from the velocity equation,

$$k' = \text{const. } e^{-E/RT}$$

the rates of the two reactions should be in the ratio $e^{-12000/2(553)} = 1:340$, instead of being equal.

An additional hypothesis is therefore necessary beyond the simple Arrhenius law. One possibility would be that, besides the energetic requirements, an additional requirement would be necessary to secure the change of the adsorbate to its end-state; for example, if to produce the CO-reaction an intermediate state of definite geometrical arrangement (a phase) was more seldom obtained than that for the CO_2-reaction the result might be explained.[12] The second case mentioned above, the dehydrogenation or isomerization of allyl alcohol [356] would also be susceptible to the same explanation.

[355] C. N. Hinshelwood, H. Hartley and B. Topley, *Proc. Roy. Soc.*, A **100**, 575 (1922).
[356] F. H. Constable, *Proc. Roy. Soc.*, A **113**, 254 (1927).

Influence of Catalyst Preparation: There are, however, a series of researches, especially on the decomposition of ethyl alcohol, which indicate an apparently simpler and more generally applicable explanation, one which also is plausible as a result of our previous conclusions. Thus, Adkins and Lazier on zinc oxide,[357] Bischoff and Adkins [358] and also Adkins and Millington [359] on titania, found that the ratio of dehydration to dehydrogenation, that is the ratio C_2H_4: H_2, is very dependent on the conditions under which the catalyst is prepared. Cremer [360] finds the same result on the oxides of the rare earths, although in these cases the activation energies of both reactions are markedly similar. It is difficult to see how the probability of decomposition of identical adsorbed molecules could be differently influenced in both directions by the previous history of the catalyst.

Influence of Poisons: Still more convincing, however, are the findings of Hoover and Rideal [243] with thorium oxide, which also catalyzes both reactions. Not only have the two reactions different temperature coefficients in spite of similar velocities, but, above all, the dehydration process may be selectively poisoned by water, acetaldehyde or chloroform, whereas the dehydrogenation continues to occur. As we shall see in the next section, the poisoning consists in a displacement of the substrate from the surface. As the substrate is displaced with predominant effect on one of the reactions, it is to be concluded that the two reactions occur on different parts of the surface, a result which is very plausible, also, in the light of dependence of the ratio of reaction on the preparation of the contact mass.

Influence of Reaction Pressure: With this conclusion, the results which Hoover and Rideal obtained with the same reaction and the same catalyst preparation at low pressures, are also in best agreement. In this case, the ratio was displaced in favor of ethylene formation. The explanation is that this reaction suffers a retardation due to its displacement by its reaction products. We have already seen that Dohse found (page 229) that water exerted such an effect. On thoria it is possible, though not proved, that ethylene may also inhibit. On lowering the pressure, the retarding adsorption of the products diminishes, but this is only noticeable kinetically on that surface which catalyzes the retarded reaction, not on the other. It is also in favor of this explanation that the apparent activa-

[357] H. Adkins and W. Lazier, *J. Am. Chem. Soc.*, **48**, 1671 (1926).
[358] H. Adkins and F. Bischoff, *ibid.*, **47**, 807 (1925).
[359] H. Adkins and P. Millington, *ibid.*, **51**, 2449 (1929).
[360] E. Cremer, *Z. physik. Chem.*, A **144**, 231 (1929).

tion energy decreases at lower pressure since λ_B (page 237) more or less drops out of the activation energy.

Selective Activity and Adsorption: One might, with Taylor,[280] generalize this point of view and explain the selective activity of a catalyst or its active fraction of surface by a selective adsorption from gas mixtures, especially since we already know of such a selective adsorption on different areas of the surface, even in simple reactions (page 231). Thus, the fact that the reaction,

$$CO + 3H_2 = CH_4 + H_2O,$$

proceeds well on nickel, and not on copper, may possibly be explained on the basis that, as is well known, carbon monoxide is strongly adsorbed on copper and so poisons the reaction. (It may be, however, that the degree of activation of the carbon monoxide is involved. Tr.)

Also, in the case of selection from successive reactions this point of view is useful, inasmuch as a protective poison may stabilize an intermediate product.[361] We have already mentioned such a mechanism in the case of ethylamine. The action of sulphur on a mixed methanol catalyst is another, clearer case, since here only the Fe_2O_3 surface and not the ZnO surface is poisoned.

Sabatier [362] and Hara [363] point out that, in cases of greater specificity in organic chemistry, the assumption of specific intermediate compounds is more suggestive. This means, however, only a restriction of selective adsorption to the catalytically active adsorption due to chemical forces.

In heterogeneous catalysis, as in homogeneous catalysis, besides a selectivity with respect to the reaction there is a specificity with respect to choice of substrate. For example, in reactions of substrates with optically active components, one component is preferentially catalyzed at an optically active contact mass. Bredig and Gerstner [363a] showed this in the synthesis of mandelic nitrile from benzaldehyde and hydrocyanic acid at a catalyst surface formed by anchoring the catalytically active diethylamine group on optically asymmetric cellulose fibres, the asymmetry of which promotes directive asymmetric change. Bredig, Gerstner and Lang [363b] have recently extended this asymmetric catalysis with success to other catalyst bases on cellulose and to nitrile formation from other alde-

[361] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.*, A **97**, 262 (1920).
[362] P. Sabatier, *J. Ind. Eng. Chem.*, **18**, 1005 (1926).
[363] T. Hara, *Mem. Coll. Sci. Eng. Imp. Univ. Kyoto*, A **9**, 405 (1926).
[363a] Bredig and Gerstner, *Biochem. Z.*, **250**, 414 (1932).
[363b] Bredig, Gerstner and Lang, *Biochem. Z.*, **282**, 88 (1936).

hydes. Schwab, Rudolph and Rose [363c] simultaneously obtained specific dehydration of optically active butyl alcohols at a catalyst composed of a metal and a quartz lattice which has the asymmetric activity. This action, therefore, was effected without the help of an asymmetric carbon atom. Since with *one* metal the catalytic oxidation promoted the opposite rotation to that obtaining in the dehydration process it follows that, in this case, it is not only a preference as to adsorption but actually a preferential chemical activation of the substrate that is involved.

Catalyst Poisons

We have already made use of a concept that has proved very fruitful in the study of surface structure, that of poisoning. Under this general term are included all the phenomena by which the presence of any substance whatever in the system produces a smaller catalytic reaction velocity than that obtaining in its absence. Poisoning may be regarded as " negative catalysis," a term which is also suggested by the fact that, oftentimes, very small amounts of a poison produce very considerable effects. We shall, however, consider the phenomenon at this point as poisoning, because, later, it will be necessary to ascribe to " negative heterogeneous catalysis " the case in which the negative catalyst is present in a different phase from the substrate whereas here it is a poisoned positive catalyst which is of interest. We are dealing, therefore, with a case, analogous to those considered in the study of homogeneous systems (pages 78 and 168), of the removal of a positive heterogeneous catalyst. This phenomenon has been as fruitful for the theoretical study of positive catalysis as it is, on the other hand, important in practice. In the latter, one has either to fight against poisoning as harmful to the catalyst or can utilize it for " protective poisoning."

Types of Poisons: For purposes of convenience two types of poisoning are recognized, " permanent " and " temporary." [364] Permanent poisoning occurs when, after removal of the poison from the reaction mixture, the velocity does not recover its normal value. It is caused, for example, by volatile silicon compounds in the ammonia oxidation process on platinum, by sulphur compounds in ammonia synthesis on iron and in hydrogenation processes employing nickel. Temporary poisoning, on the other hand, disappears if, after the poisoning, one begins to operate with poison-free gases, because the poison then leaves the catalyst without having changed it or its

[363c] Schwab, Rudolph and Rose, *Naturwiss*, 20, 362 (1932); *Koll. Z.* 68, 157 (1934); *Z. angew Chem.*, 48, 73 (1935).

[364] E. K. Rideal and H. S. Taylor, Catalysis in Theory and Practice, 2nd edition, pp. 127 et seq. Macmillan and Co., London, 1926.

capacity. The poisoning of the hydrogen-oxygen reaction on platinum by carbon monoxide, studied by Faraday, belongs to this type, as does also the poisoning of ammonia synthesis by oxygen and its compounds, shortly to be considered. Above all, those cases with which we have already become acquainted in our discussion of velocity equations, in which a reactant or product retards proportionately to its amount present, are to be considered as cases of temporary poisoning. Increase of the velocity of gas flow, that is to say, diminution of the partial pressure of the poison decreases all such retardations.[283]

Permanent poisoning is principally due to formation between catalyst and poison of a compound which covers the former superficially with a non-catalytic coating. This accounts for the fact that, on nickel and copper, the velocity of the hydrogen-oxygen reaction falls abruptly, practically to zero, at that moment at which the skin of oxide which is being formed covers the metal completely.[308, 309] For the same reaction on silver and on gold, Chapman, Ramsbottom, and Trotman [365] were able directly to confirm this conclusion, in that, by pumping off the oxygen poison, they observed a rise in the activity below a quite definite oxygen pressure, the dissociation pressure of the oxide skin, of the order of magnitude of 0.001 mm.

This shows immediately that the expression " compound with the catalyst " must have a broader significance than stoichiometric, crystallizable compounds. Surface compounds can even be stable under conditions in which the corresponding compact compound is no longer capable of existence, because of their differently arranged binding forces. Gold oxide is even unstable at atmospheric pressure and room temperature and, according to Landolt-Börnstein Tables, the dissociation pressure of silver oxide is one hundred times that of the pressure 10^{-3} mm. employed in the above experiments. On the other hand, the expression " permanent " can only be defined relatively, namely as to irreversibility under the conditions of the catalysis, since we have seen, in the last example, that even the surface — or adsorption — compound can decompose under suitable conditions.

Actually, temporary poisoning can first be produced if the poison-complex forms a stable compact compound, less stable than the surface compound. This is the case, as many investigations show, in the retardation of ammonia decomposition on iron by water vapor, oxygen and carbon monoxide, a fact which is employed in the process of coking in iron retorts to protect the yield of ammonia. In the reducing atmosphere of the ammonia, all these gases immediately form water vapor so that we only need to con-

[365] D. L. Chapman, J. E. Ramsbottom and C. G. Trotman, *Proc. Roy. Soc.*, A **107**, 92 (1925).

sider this latter. A. Schmidt [366] was able to show that the poisoning action of the water vapor on iron catalysts stopped when the water vapor to hydrogen ratio was lower than that at which the reaction,

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O,$$

began to take place in the forward direction as written. Below such ratios, the skin of the previously stable oxide was reduced. The same holds true for hydrogen chloride poisoning due to chloride formation. The observations of Almquist and Black [367] on "promoted" iron catalysts are of interest, showing that the more stable surface compound formed with such catalysts can only be reduced in systems containing still smaller partial pressures of water vapor. We shall return to this point later (page 302).

In most cases of temporary poisoning it is a question, however, of a quite specific surface compound, in other words, of especially strong adsorption of the poison so that the reactants are displaced from the catalytic areas of the surface. With such processes, we shall now, in the main, be concerned.

Characteristics of Poisons: The substances which exert such a poisoning effect are not only different for different catalysts but also vary for different reactions. Water formation is retarded by hydrogen at iron-noble metal alloy surfaces and by oxygen at nickel-noble metal alloys.[368] Water, in high concentrations, poisons the combustion of carbon monoxide at various surfaces.[369] That sulphur compounds are dangerous poisons for most metallic catalysts has already been mentioned. This holds to a still greater degree for arsenic compounds, for example, in the contact sulphuric acid process.

It is a quite characteristic fact in many cases and, for example, in the two cases last mentioned, that even very minute amounts of a poison suffice to displace the substrate entirely from the catalytically active areas of the surface. In other words, the reaction is practically completely inhibited. This depends upon an especially excessive heat of adsorption of the poison on the contact mass in question, as would be expected, for example, on chemical grounds, with sulphur and arsenic on metals.

Adsorption on Poisoned Surfaces: If the interpretation of poisoning as a preferential adsorption is correct, it must necessarily follow that the presence of poisons will measurably influence adsorption itself. This is actually the case as revealed in circumstances which are favorable for measurement.

[366] A. Schmidt, *Z. angew. Chem.*, **38**, 1146 (1925).

[367] J. A. Almquist and C. A. Black, *J. Am. Chem. Soc.*, **48**, 2814, 2820 (1926).

[368] H. Remy and H. Gönningen, *Z. anorg. allgem. Chem.*, **148**, 279 (1925); **149**, 283 (1925). H. Remy and B. Schaefer, *ibid.*, **136**, 149 (1924).

[369] W. A. Bone, *Proc. Roy. Soc.*, A **112**, 474 (1927).

Maxted [370] demonstrated a diminution of adsorption by palladium black from solutions, the diminution being proportional to the content of the adsorbent in poison. Under better experimental conditions, involving adsorption from the gas phase, Pease and Stewart [371] found the same thing, the adsorption of hydrogen by copper being measurably diminished by carbon monoxide, which poisons the hydrogenation of ethylene.

Kinetics on Poisoned Surfaces: We have, however, already indicated that direct adsorption measurements can only reproduce imperfectly the conditions at the catalytically active areas of the surface. It would, therefore, be more favorable for a demonstration of preferential adsorption by the poison if we possessed a criterion which revealed the characteristics of poisoning by adsorption only at the active centers of the surface. Such a criterion is to be found in the fact that the decrease in reaction velocity itself obeys a Langmuir adsorption isotherm for the gaseous poison. We may recall, from our presentation of the self-retarding reactions, that this is actually the case (Case I2, pages 224, 228 et seq.). As regards the retardation by poisons foreign to the reaction we may refer to the researches of Constable [302, 295] in which the dehydrogenation of ethyl alcohol on copper is retarded by water acetone and benzol, to an increasing degree in the order given, and obeying our equation I2*c*, page 226. Also in the work of Pease and Stewart [371] just mentioned, the residual velocity of hydrogenation of ethylene in the presence of carbon monoxide is representable by reaction on the area of the surface left free by the strongly adsorbed carbon monoxide. That is, *ceteris paribus*, it is proportional to

$$1 - \sigma_{CO} = \frac{1}{b_{CO} p_{CO}}.$$

The poisoning of the water gas reaction,

$$H_2O + CO = CO_2 + H_2$$

by hydrogen sulphide on iron contact masses, studied by Evans and Newton [372] behaves similarly. Other, different examples might also be assembled.

Poisoning and Temperature: From the nature of poisoning thus more or less defined, certain conclusions may be reached concerning the temperature coefficient of poisoned reactions. In the first place, a permanent poison, which simply eliminates a definite portion of the active area in the

[370] E. B. Maxted, *J. Chem. Soc.*, **115**, 1050 (1919); **117**, 1280, 1501 (1920); **119**, 225, 1280 (1921); **121**, 1760 (1922); **127**, 73 (1925).

[371] R. N. Pease and L. Stewart, *J. Am. Chem. Soc.*, **47**, 1235 (1925).

[372] R. M. Evans and W. L. Newton, *J. Ind. Eng. Chem.*, **18**, 513 (1926).

temperature range employed, leaves the activation energy of the remainder of the surface unchanged. It influences the velocity but not the temperature coefficient. Constable [373] has demonstrated this directly in the dehydrogenation of alcohols by copper poisoned by the fusel oil in impure amyl alcohol. With temporary poisoning, the situation is otherwise, since, in this case, the fraction of the surface free from poison changes with temperature, at least in those cases where an adsorption equilibrium (or equilibrium surface compound) exists between poison and surface. For such a case, the temperature dependence is already known; it is the same as that of retarded reactions in the previous discussion of kinetics. The apparent activation energy E_a is equal to the true activation energy E, plus the heat of adsorption of the poison,[364] so long as the adsorption is strong. In other cases, the temperature dependence will be more complicated (see page 239 and reference 302).

Poisoning and Surface Area Affected: A further consequence of the concept of poisoning as a preferential adsorption must be that, for complete poisoning, the amounts of different poisons required must bear a simple molecular ratio to one another; complete poisoning implies a covering of the same areas of the surface. This requirement is also fulfilled. Ghosh and Bakshi [374] find that the dehydrogenation of methanol and formaldehyde at cerium-promoted copper is poisoned by carbon disulphide, chloroform and bromine in such a way that, for complete poisoning, approximately equal numbers of atoms of sulphur, chlorine and bromine are necessary. It should be emphasized that the concept of " complete poisoning " is not susceptible to rigorous definition; but, on the area in question, near to adsorption saturation, the amount of poison adsorbed does not greatly change, so that this crude definition still implies a sharply defined limiting amount of poison.

Other consequences of our concept are, however, in no way confirmed by experiment, and it is precisely these which give poison.phenomena their especial interest both technically and particularly in the study of the structure of catalysts.

It was evident already to Maxted [370] that the diminution of adsorption of the reactants due to poisoning was always many times less than the diminution in reaction velocity. Pease [375] found the same thing. An example, frequently cited, is to be found in the work of Pease and Stewart.[371] Mercury vapor decreased the adsorption of ethylene on copper to 80 per cent of normal, hydrogen to 5 per cent of normal, the velocity of hydrogenation,

[373] F. H. Constable, *Proc. Camb. Phil. Soc.*, **22**, 738 (1925).
[374] J. C. Ghosh and J. B. Bakshi, *J. Indian Chem. Soc.*, **6**, 749 (1929).
[375] R. N. Pease, *J. Am. Chem. Soc.*, **45**, 2235 (1923).

however, to 0.5 per cent of normal. The mere reduction in adsorption ($0.8 \times 0.05 = 0.04$) would lead one to expect a velocity 4 per cent of normal. In a case studied by Griffin [376] the discrepancy is even more pronounced.

Although this fact alone indicates that, for the definition of the reaction, the total measurable adsorption is not important but only the adsorption on certain definite areas, the same emerges more strikingly from a consideration of the adsorption isotherms of carbon monoxide, in the researches of Pease and Stewart.[371] These isotherms can be calculated from the diminution in the velocity of hydrogenation as was shown by Constable.[377] It is found that the adsorption constant for the poison, b, is not constant from the beginning, but first shows falling values; that is to say, the poison first saturates centers of exceptionally strong adsorptive capacity before the average catalytically active areas with constant b are reached.

Kaeb,[378] in the laboratory of Bredig, has shown that the electrochemical potential of poisoned platinum sponge is more noble than that of completely active sponge. The potential displacement varies from 3 millivolts when saturated with gas to 200 millivolts in the presence of inorganic salts. This variation shows that, with different poisons, areas of progressively changing solution tension are put out of action, that, therefore, a progression of areas is present on the surface.

Selective Poisoning: The qualitative differentiation of the catalytically active surface is still more definitely indicated by the phenomena of selective poisoning, which has already been recognized as of fundamental importance in the discussion of selective catalysis (page 268). Willstätter and Hatt [379] found that thiophene-containing benzol cannot be hydrogenated on platinum, whereas an aliphatic unsaturated hydrocarbon in the same solution, while hydrogenated slowly, was still completely hydrogenated. According to this, thiophene poisons the hydrogenation of the aromatic ring (also that of naphthalene) markedly more strongly than that of the open chain. The observations of Kubota and Yoshikawa [380] on nickel are quite analogous. The most active areas which hydrogenate aromatic rings are poisoned by thiophene, without the catalyst losing its capacity to hydrogenate olefines. Ethyl sulphide destroys this latter capacity but the reduction of nitrobenzene is still possible, this in turn being destroyed by hydrogen sulphide.

[376] C. W. Griffin, *J. Am. Chem. Soc.*, **49**, 2136 (1927).
[377] F. H. Constable, *Proc. Camb. Phil. Soc.*, **23**, 832 (1927).
[378] G. Kaeb, *Z. physik. Chem.*, **115**, 224 (1925).
[379] R. Willstätter, and D. Hatt, *Ber.*, **45**, 1471 (1912).
[380] B. Kubota and K. Yoshikawa, *Sci. Pap. Inst. Phys. Chem. Res.*, **3**, 223 (1925).

Vavon and Huson [381] have also studied such phenomena systematically. Rideal and Wright [382] found a variation in the surface even of charcoal by poisoning. Ghosh and Bakshi [374] found that small amounts of carbon disulphide and chloroform do not poison the dehydrogenation of methanol on cerium-promoted copper but do poison the dehydrogenation of the formaldehyde produced, thus protecting this latter. Other examples of protective poisoning and their significance have previously been discussed (page 270).

The conclusion which Taylor,[287] principally, has drawn from these facts as to the chemical variability even of surfaces composed of a single atomic species is therefore unavoidable. Precisely with respect to the phenomena of poisoning, it would be difficult to understand, and perhaps a backward step from the standpoint of teaching and research, if one should wish, with Sauter,[229] to declare that these results based on the catalytic function were not definitive of the catalyst structure, and " to derive the variability of reaction possibilities from a closer study of (ad-)sorption." This is especially so because, as we have already seen, adsorption reproduces this variation only feebly, if at all.

In the next chapter, we shall become acquainted with the results and hypotheses to which a comprehensive review of all the observations on adsorption, kinetics, on selectivity in catalysis and on poisons, together with allied theoretical considerations, have already led at the present time. We shall see that a really unified picture, at least in outline, can already be presented.

[381] G. Vavon and A. Huson, *Compt. rend.*, **175**, 277 (1922).
[382] E. K. Rideal and W. M. Wright, *J. Chem. Soc.*, **127**, 1347 (1925).

CHAPTER XV

THE STATE OF A CATALYST

In the first instance, the changes in catalytic properties of a substance that may be achieved by means of the method of preparation or preliminary treatment must be discussed. Numerous investigations indicate that as fine a division of the contact mass as possible is favorable to its activity, is, indeed, often a practical necessity. Thus, platinum sponge, finely divided copper, and pyrophoric nickel are good catalysts for many reactions whereas foil or wire of the same material is completely inactive. This at once suggests that such phenomena are to be ascribed simply to the greater surface area of fine powder. A simple consideration shows that, with particles somewhat similar geometrically to one another, the surface per gram of material is inversely proportional to the diameter of the particle. The concept of the influence of surface extension can, therefore, be tested quantitatively by comparing the measured particle size with the activity of different preparations.

Particle Size and Activity: For the measurement of particle size, different methods may serve. Lottermoser [383] makes use of the microscopic method and actually obtains an increase of activity with decreasing particle size. O. Schmidt [316] determines directly the surface of active nickel preparations by measuring their velocity of solution in acids, comparing the results, by means of the Nernst-Brunner law, with the solution of compact nickel and thus finds that the velocity of hydrogenation increases simultaneously, and, in his view, proportionally to the specific surface. Hüttig makes use of sedimentation analysis for comparison of particle size and catalytic activity of oxides.[383a] We shall return to these researches.

In the cases cited, it is a matter of particles of the order of magnitude of 10^{-4} cm. With still finer material, an X-ray method is applicable which permits particle size to be deduced from the diffuseness of the Debye-Scheerer interference patterns. It depends upon the fact that, owing to disturbances in the lattice and heat motion, the interference patterns are not sharp when there are too few planes of the lattice present. The upper limit of this method lies around 100 atom layers of the crystallite and there-

[383] A. Lottermoser and W. Eichler, *Z. Elektrochem.*, **35**, 610 (1929).

[383a] Hüttig, *Koll. Beih.*, **39**, 277 (1934).

fore around 10^{-6} cm.[384] The method has been worked out especially by Brill and Pelzer.[385] As an example, an older investigation of Levi and Haardt [386] may be cited. These authors found, in this way, that platinum sponge decomposed hydrogen peroxide more slowly the larger the particle size. In one case, that of skeletal contact masses of nickel as investigated by Schwab and Zorn (see p. 221), it could thus be demonstrated that the catalytically active portions of the catalyst are, from the X-ray crystallographic point of view, no longer crystalline, containing fewer than about six atom layers connected together.

The adsorption capacity for gases should be to some extent a measure of surface development. Although Paneth and Vorwerk [238] were able to determine the surface of various powders by measuring the adsorption of dyes, the method is one which, as yet, has found no application in the case of catalysts. One of the difficulties is the choice of a gas which will be adsorbed on the whole surface thus giving a true measure of surface area with different preparations. The data on gas adsorption by catalysts abundantly illustrate this difficulty.[386a] In the single case of platinum, according to investigations of Benton [386b] indications were present that the adsorption of oxygen and carbon monoxide gave a measure of surface area. Researches of Schwab and Schultes [386c] indicate the applicability of the method.

Sintering: One field in which, however, the diminution of gas adsorption with decrease in surface has been very definitely demonstrated is that of the " sintering " of catalysts. By this term we do not mean, as is customary in other connections, the packing together of a powder by means of surface fusion, but rather the recrystallization of small particles and finely divided material to form coarser material, far below the melting point, by reason of thermal exchanges of position and self-diffusion. Such processes are especially facilitated in the surface by reason of the weaker binding of the atoms there.

Catalysts, more particularly the very active materials of industry, are, thermodynamically, highly unstable systems of loose surface structure and great surface development, mostly prepared by chemical methods, such as reduction and precipitation, at as low temperatures as possible. If such

[384] R. W. G. Wyckoff and E. D. Crittenden, *J. Am. Chem. Soc.*, **47**, 2866 (1925).

[385] R. Brill and H. Pelzer, *Z. Kristallogr.*, **68**, 387 (1928); **72**, 398 (1930).

[386] G. R. Levi and R. Haardt, *Atti. Acad. Linc.*, (6) **2**, 419 (1925); (6) **3**, 91, 215 (1926); *Gazz Chim. Ital.*, **56**, 424 (1926).

[386a] H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, **43**, 1273 (1921).

[386b] A. F. Benton, *J. Am. Chem. Soc.*, **48**, 1850 (1926).

[386c] Schwab and Schultes, *Z. angew. Chem.*, **45**, 341 (1932).

systems are exposed to high temperatures and especially to over-heating while in use, a more stable surface structure is produced, the larger crystallites grow at the expense of the more volatile smaller particles, the rough surface becomes smoother and the activity falls. (See E. Fajans.[283f]) It is for this reason that, in industry, especially with exothermic catalytic reactions, and these are the majority, a suitable balance of conversion and heat transfer away from the contact mass is so important.

These processes of sintering are also a further fruitful source of knowledge concerning surface structure. Is the decrease in activity due to sintering proportional to the decrease in adsorption and to the decrease in surface, or are conditions similar to those in the case of poisoning? Actually the latter is the case. For example, Rudishill and Engelder [387] found that, on sintering, titanium oxide was poorer for alcohol decomposition but that the dehydrogenation was affected to quite a different degree than the simultaneous dehydration. Sabatier [329] was able, by heat treatment during the preparation of a catalyst, successively to eliminate various functions of one and the same catalyst. Taylor [280, 281] has collected numerous other examples of this kind. It is apparent that centers of different types sinter to different degrees.

Activity and Method of Preparation: In close relation to the data cited are experiments in which the activity of the original catalytic material is dependent on the method of preparation, phenomena especially investigated by Bischoff and Adkins.[358, 359] The catalytic activity of a zinc or titanium or aluminum oxide depends in magnitude and selectivity on whether the oxide was prepared from the oxalate, or the nitrate or the carbonate, etc.[387a] Bischoff and Adkins seek to account for this by the differences of spatial arrangement in the pseudo-lattices obtained, starting out from a point of view similar to that of Balandin-Burk already discussed. However, the different starting material involves a different temperature of preparation or decomposition and, therefore, also a different ratio of velocities of nuclei formation and nuclear growth, so that the effect would be present in the development of a normal lattice and would not be fundamentally different from that obtaining as a result of a subsequent sintering.

That such differences in the formation of lattices can, however, result in quite important differences in catalytic and other properties of the material is easily understandable. Not only the size of the crystallites

[387] W. A. Rudishill and C. Engelder, *J. Phys. Chem.*, **30**, 106 (1926).

[387a] See, also, the researches on zinc oxide by G. Hüttig and his collaborators: For example, Hüttig and Brüll, *Ber.*, **65**, 1795 (1932); Steiner and Hüttig, *Koll. Z.*, 68, 253 (1934); Hüttig, *Koll. Beih.*, **39**, 277 (1934) in which further literature is given.

but the development of their several faces, and their porosity can vary; but, above all, the thermodynamic energy content is determined by the degree of division and surface development. Catalytically, such effects can result in marked changes in reaction direction. Methanol is mainly converted to methyl formate by zinc oxide prepared from the oxalate, and to carbon monoxide and hydrogen by zinc oxides ex carbonate. The differences arise mainly thus, that, before the formation of the final lattice, active, amorphous intermediate stages are developed. The final lattice is of itself not different but only in the morphological factors just mentioned. G. F. Hüttig and his co-workers have busied themselves with these relations in a large series of publications.[387a]

A further contribution to this problem is made by Kohlschütter [387b] in his studies of pseudo-morphic ferric oxides prepared by topochemical hydrolysis from ferric sulphate, the catalytic activity of the product being tested in the decomposition of hydrogen peroxide solutions. The observations of Rummel [334b] on the activation of adsorbent charcoals for para-hydrogen conversion at low temperatures belong in the same category. Also, the frequently observed activation of catalysts while in use [387c] is pertinent to this problem.

Active Centers

In the preceding paragraphs we have become acquainted with the final milestone in a series of observations all of which lead to one and the same fact. We have already indicated this fact at least in outline and have utilized it successfully in the interpretation of the observations. It is the fact of the "variability of the surface," of the presence of different regions or positions, or to use the term which has been introduced, the presence of different "active centers."

The experimental bases are the variability of the heat of adsorption with area of surface covered, the adsorption of binary mixtures without mutual displacement, the gradual progressive variability of adsorption of the same gas in different reactions and different regions of pressure, selective catalysis, selective poisoning and sintering, and, finally, the abnormal sensitivity of catalysis itself towards poisons, method of preparation and sintering, as compared with the sensitivity of surface extension and adsorption.

[387b] H. W. Kohlschütter, *Z. anorg. Chem.*, **213**, 189 (1933); Kohlschütter and Siecke, *Z. Elektrochem.*, **39**, 617 (1933); **41**, 851 (1935).

[387c] Zawadsky and Modrzejewsky, *Rocznikow Chemji*, **11**, 505 (1931) deal with ammonia decomposition activating iron. Zawadsky and Badzynsky, *ibid.*, **11**, 158 (1931) discuss nitric oxide on platinum.

The Concept of Active Centers: Taylor has done a great service in collecting all these facts in a series of publications [280, 281] and in having produced among individual points of view a concrete picture of the catalytic surface. He postulates, for the outer surface of a real solid body, that in it, as Fig. 35 shows, there are present not only atoms which only impinge on the gas phase in one direction (atoms in the plane surface) but also edge atoms with two, corner atoms with three and peak atoms with four or five valences projecting into space and which are, in virtue of their position, able in marked degree to adsorb gases, to deform or to dissociate their molecules in the manner found necessary in preceding sections.

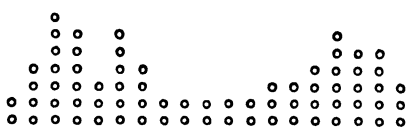


FIG. 35. Diagrammatic Representation of a Catalyst Surface (Taylor).

This principle obviously contains all points of view which have hitherto been found necessary for the interpretation of the various anomalies. We can thus understand that the heats of adsorption are different from area to area, that reactions of different kinds can occur on different atomic arrangements, that a retarding agent may influence one reaction strongly, another reaction, occurring on other atoms, but slightly, and above all, we can understand how heat treatment affects the different centers so differently. It will be the most active peak atoms which, by sintering, will first free themselves from the lattice association and settle down in more stable positions.

We have before us, therefore, in Taylor's hypothesis, an immediate explanation of a large and diverse complex of phenomena, which, at least, in teaching and research, must be extraordinarily fruitful. To deny active centers and to ascribe all indications pointing to such, to an " admixture capable of chemosorption " (Sauter [229]) is merely a change of nomenclature. Equally untenable, it seems to us, is the standpoint of Schmidt,[387d] according to which, fissures and pores of approximately atomic dimensions are the seat of catalysis, because the hydrogen is ionized in the *interior* of the contact mass (see page 254). For, in those places to which large organic molecules of substrate can penetrate, the properties of an undisturbed lattice cannot be operative. It can be objected that we are concerning ourselves with a purely qualitative principle only, which contains as many degrees of freedom (over and above the ideal lattice) as may be needed to include all the anomalies in the interpretation. This is certainly true, but the more numerous anomalies of this kind and importance, the more direct is the indication of

[387d] O. Schmidt, *Z. physik. Chem.*, A **165**, 133 (1933); *Z. Elektrochem.*, **39**, 834 (1933). *Ber.*, **68**, 1098 (1935).

variable activity and the closer will be the quantitative framework which is placed around the qualitative picture.

Apart from the comprehensibility, theoretically, of the activity of " free lattice valences," we have now, in the investigations of Frankenburger and Mayrhofer [335] and of Mittasch and Frankenburger,[336] actual proof that wholly or even partially isolated atoms, especially the latter, are capable of chemical effects such as the adsorption of hydrogen and nitrogen which the compact material of the lattice is incapable of achieving to a measurable extent. A direct proof of Taylor's theory is thus obtained.

Distribution of Active Centers: We must now immediately remove the misconception that the assumption of " active centers " signifies that catalytic reactions can never, in principle, occur at plane lattice surfaces, and that only the most loosely bound atoms form the actual catalyst. Taylor, himself,[274] rejects such an interpretation and points out that all the atoms of the surface share in a distribution of variable energies, unsaturation and catalytic activity. The prerequisite to a quantitative development of the idea of active centers would therefore be the determination of this distribution in individual cases; that is to say, a determination of the number of atoms, ions or the like in a surface, which possess a value, lying between certain defined limits, for any particular property such as potential energy, heat of adsorption, reaction velocity or the like. Taylor [274] has had such measurements made and gives, for a particular iron contact mass, the following data for heats of adsorption of ammonia with increased coverage of the surface.

TABLE XXXV — HEATS OF ADSORPTION OF AMMONIA

Ccs. adsorbed	2	4	6	8	10	12	14
λ_{NH_3} in kilocals.	18	16	14	12.5	11.3	10.5	9.9

The adsorbed amount of ammonia can here serve as a measure of the number of iron atoms adsorbing, whose energy progressively changes as does that of the heat of adsorption. We notice first that that portion of the atoms which liberates the highest heat of adsorption on saturation, in other words the most active centers, are only a very small fraction of the total number. It is thus understandable that the reaction velocity will be much more strongly affected by sintering or by poisons than is the adsorption.

While such statistics refer to the adsorbing surface as a whole the reactions studied by Dohse,[303] in unimolecular layers, without gas phase, give directly the progression of active centers on which measurable reaction occurs. The adsorbed alcohols decompose (page 230) at a rate proportional to the amounts adsorbed, that is they follow the first order rate, and the reaction constant thus observed is a measure of the mean activity of the active

centers still covered at that time. In Fig. 36 are given the measurements and interpolations of Dohse for the unimolecular decomposition of adsorbed isopropyl alcohol on bauxite.

This result, compared with that of Dew and Taylor [387e] on the ammonia iron system, is somewhat astonishing. We see that the reaction constant is constant up to a certain density of adsorption which is independent of temperature and that then a rapid fall occurs. There exists therefore a quite accurately calculable number of centers of equal and high reaction velocity. The break in the curve presumably occurs at that amount of adsorption which corresponds to saturation of this type of centers. With still higher adsorption, the centers of smaller and continuously distributed activity become noticeable.

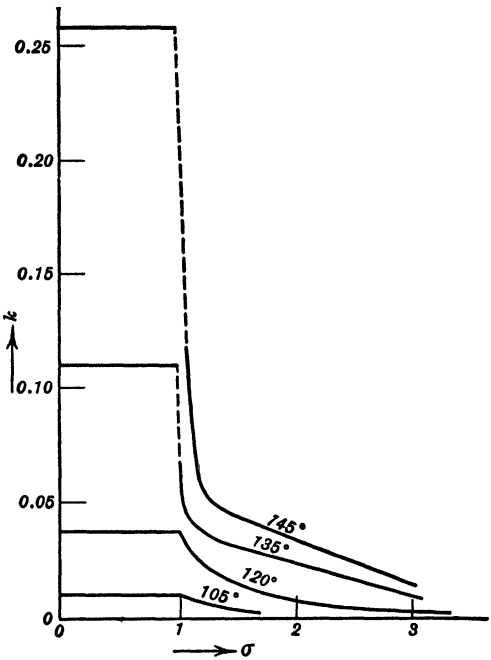


FIG. 36. Velocity Constant of the Decomposition of Isopropyl Alcohol Adsorbed on Alumina as a Function of Film Thickness (Dohse).

Uniform Activity of Centers Operative: There seems to be a discrepancy here, actually not limited to these two series of measurements but extending to the whole field of interface chemistry. The results of Dohse's work correspond wholly to that which we have assumed in the mathematical treatment of the reaction kinetics (page 222), and that which we really had to assume: a constant k and a constant b for each reaction, that is to say, only one type of active centers with identical properties. This is the picture we always obtain when we employ catalytic reactions themselves for measurement. If, on the other hand, we measure adsorption, as in the preceding table, we always encounter a more or less numerous set of values for the energies. This contradiction in the two different conclusions concerning the distribution can only be eliminated if we say: Of the many types of center that are present in the surface and which adsorption measure-

[387e] Dew and Taylor, *J. Phys. Chem.*, 31, 277 (1927).

ments reveal to us, there is, for a given reaction, only one kind kinetically so overwhelmingly active that it is possible always to describe the kinetic results by means of a uniform surface. This must not be taken as meaning that the other types of center do not act catalytically at all; it only means that a narrow region of positions exists in which the atoms act so efficiently that the average effect observed only differs little from that which the most active atoms alone effect. Only when these are poisoned, do other centers with changed b become important as is shown in Constable's calculations [377] of the results of Pease and Stewart.[371]

This predominance of the active centers is also understandable from the theoretical standpoint. The ideas leading to this conclusion derive mainly from Constable,[388] and are here given with some changes which go back to a research of Cremer and Schwab.[389] Let the number of centers dn, at which the activation energy lies between E and $E-dE$ be given by a function $F(E)$, yet to be determined, such that

$$dn = F(E)\, dE.$$

Let the contribution, dk, of these centers to the velocity constant be given, in accord with the Arrhenius equation, by the expression

$$dk = c \cdot e^{-E/RT}\, dn = c \cdot F(E) e^{-E/RT}\, dE.$$

E may vary between a lower limit E_1 and an upper limit E_2. It is necessary that a lower limit exist; otherwise the velocity, according to the subsequently derived form of $F(E)$ would be infinite; its importance will later be noted. An upper limit must exist since even the most inactive centers considered must also produce reaction acceleration.

The observed activation energy, that is to say, the mean value of E for all the reacting substrate molecules (not for all the centers on account of their varying weights) is then given by

$$\overline{E} = \frac{\int_{E_1}^{E_2} E dk}{\int_{E_1}^{E_2} dk} = \frac{\int_{E_1}^{E_2} E\, F(E) e^{-E/RT}\, dE}{\int_{E_1}^{E_2} F(E) e^{-E/RT}\, dE}.$$

To evaluate this, a knowledge of the function $F(E)$ is necessary. Consideration, even, of Taylor's data on the heat of adsorption on iron seems to suggest that F has the character of an exponential function. Also,

[388] F. H. Constable, *Proc. Roy. Soc.*, A **108**, 355 (1925).

[389] E. Cremer and G.-M. Schwab, *Z. physik. Chem.*, A **144**, 243 (1929); G.-M. Schwab, *ibid.*, B **5**, 406 (1929).

Mark's relation between heat of adsorption and adsorption volume (page 197) indicates the same thing. Such a form is also to be expected theoretically. For a general, orientating, theoretical development of F we now consider a quantity, E', according to Cremer and Schwab the "excess energy" of the active atoms as compared with the atoms in the plane surface of the lattice, or in the view of Constable, a tension energy of position. If the catalyst surface has reached statistical equilibrium at its temperature of preparation θ, and retained this equilibrium (which is probably true of catalysts which have been first heated to high temperatures), then, according to the Boltzmann relation,

$$dn = f \cdot e^{-E'/R\theta}\, dE'.$$

If, however, as is true in the case of most catalysts, the distribution in space of the atoms is a purely chance, unstable distribution, determined by the kinetic processes during their preparation, one can postulate, with Constable, that their distances from one another will be distributed about the normal distance according to a Gauss error function. A plausible relation between these distances and their potential energies (that of the normal distance being set equal to zero) leads to an equation of the form

$$dn = f\, e^{-E'/h}\, dE'$$

which differs from the previous one only in this that h has no direct relation to the temperature of preparation but merely represents a parameter of spread or deviation from the mean. In either case we arrive at an exponential distribution of the excess energy E' which we shall use in the second or more general form.

We must now relate E' with E, the true activation energy at the catalyst atom. We have already seen that the homogeneous activation energy E_h is diminished at an atom in the lattice by the heat of adsorption ${}_m\lambda_a$ of the active state at the normal lattice atom. At an atom with an excess energy E' it will be still further diminished by this amount E' since the amount represents the increased energy yield on formation of the surface compound, which is not required in the heat of deformation (Polanyi, London, page 248). Constable provides this diminution, for the sake of safety, with a proportionality factor, which only changes the constants, and these cancel later. We thus obtain

$$E = E_h - {}_m\lambda_a - E'$$

and, hence,

$$dn = F(E)\, dE = f\, e^{-(E_h - {}_m\lambda_a)/h}\, e^{E/h}\, dE = a\, e^{E/h}\, dE.$$

The distribution function F of the activation energy is thereby determined and can be inserted in the equation for E. This gives

$$\overline{E} = \frac{\int_{E_1}^{E_2} E \cdot e^{E\left(\frac{1}{h} - \frac{1}{RT}\right)} dE}{\int_{E_1}^{E_2} e^{E\left(\frac{1}{h} - \frac{1}{RT}\right)} dE}.$$

Setting $\frac{1}{h} - \frac{1}{RT} = -\frac{1}{r}$ and inserting the limits

$$\overline{E} = \frac{e^{-E_1 r}\left(E_1 + \frac{1}{r}\right) - e^{-E_2 r}\left(E_2 + \frac{1}{r}\right)}{e^{-E_1 r} - e^{-E_2 r}}.$$

Now, since $E_2 > E_1$ and, according to available measurements given later, r is positive, this expression simplifies to

$$\overline{E} = E_1 + \frac{1}{r}.$$

It is thereby shown that, even with a continuous distribution of centers, the reaction behaves approximately as though it took place on only one type of center. (Concerning the breaks in the curves of Fig. 36, see page 283.) It is further shown by consideration of the sparse numerical data that $1/r$ only causes a small correction, so that, in fact, the overwhelming part of the reaction of the most active centers of all is effected with the lower limit of the activation energy. By reason of the form of the Arrhenius equation, their small number is compensated for by their large contribution to the reaction velocity. From poisoning studies by Rideal and Wright,[382] it seems that this fraction is of the order of one per thousand of the surface. We now understand why the kinetic measurements show such good constant properties for surfaces which, from the indications of their adsorption isotherms and heats of adsorption, are quite inhomogeneous.

The question suggests itself as to how far the assumptions concerning the distribution, which lie at the basis of the whole consideration, are valid. We must expect that, in the equation

$$k = c\, e^{-E/RT},$$

which we can now employ again without restraint for the narrow region of measurably active centers, the " activity," c, apart from unimportant factors such as size of surface and the like must be given by an equation

$$c = a \cdot e^{E/h}.$$

This implies that, with a constant, that is to say, the same reaction at a similar catalyst, a large decrease in the activation energy (small E and therefore larger k) will be compensated for by a small c, in other words, a small activity (and thereby, once more, a smaller k) so that neither extremely good nor extremely bad activities within such a group of catalysts are possible.

Constable has tested this relationship with copper preparations obtained by reduction of the oxide at different temperatures. The measured activation energies for dehydrogenation of alcohol varied between 25.6 and 21.6 kilocals., while simultaneously the activity fell from 13 to 0.19, very rapidly, in agreement with the exponential form and, so rapidly that h, within the error of measurement, actually remained constant. The same relationship was found by Balandin [389a] in the dehydrogenation of various substrates at a variety of contact masses. The following table shows these results:

TABLE XXXVI — ACTIVATION ENERGIES AND h VALUES FOR VARIOUS REACTIONS

Substrate	Catalyst	Support	E(kcal.)	$2.3 \times 10^{-3}h$.
Cyclohexanone	Pt, 30%	Charcoal	23.71	2.1
Cyclohexanonimine	Pt, 25%	Asbestos	19.93	2.2
Decalin	Pt, 30%	Asbestos	18.99	2.1
Decalin	Pt, 30%	Charcoal	18.89	2.0
Cyclohexane	Pt, 25%	Asbestos	18.04	2.0
Cyclohexane	Pt, 25%	Charcoal	18.04	2.0
Decalin	Os, 25%	Asbestos	16.50	2.3
Cyclohexanonimine	Pd, 42%	Asbestos	16.25	1.9
Cyclohexane	Ni, 23%	Al_2O_3	16.23	2.0
Cyclohexane	Pd, 49%	Asbestos	15.30	2.0
Cyclohexane	Ni, 43%	TiO_2	13.70	2.1
Cyclohexanol	Pt, 30%	Charcoal	11.62	1 8
Decalin	Os, 25%	Asbestos	10.00	2.2
Decalin	Ni, 72%	Asbestos	9.99	2.2
Cyclohexane	Ni, 76%	Asbestos	9.70	1.9

In both Constable's and Balandin's experiments the catalysts were protected from sintering by the greatest precautions. If, however, the catalyst, before use, had an opportunity, due to heating or chemical change to attain an equilibrium configuration, it would be anticipated, according to Cremer and Schwab,[389] that

$$h = R\theta$$

where θ is the temperature at which the equilibrium distribution was

[389a] A. Balandin, *Z. physik. Chem.*, B **19**, 451 (1932).

"frozen," and therefore, under favorable conditions, the temperature of formation. Cremer [360] has measured the activity and activation energy of alcohol decomposition on tervalent oxides of the third group of the periodic table, and has found, for constant a, the following constant for h:

TABLE XXXVII — ACTIVATION ENERGIES AND h VALUES FOR OXIDE CATALYSTS

Catalyst	Al_2O_3	In_2O_3	Sc_2O_3	Y_2O_3	Ce_2O_3	La_2O_3
E(kilocals.)	13	23	29	30	30	32
$2.3 \times 10^{-3}h$	4.3	3.9	4.2	4.3	4.3	4.3

Although, therefore, the activation energies change from 13 to 32 and the velocities in the ratio of 1:10,000, in this case also, in which the chemical nature of the catalyst changes, h is excellently constant. Furthermore, the relation to the method of preparation seems to be fulfilled, for it follows that $\theta = h/R = 940°$ Abs. which would indicate dark red heat. Actually the catalysts were heated before use to this temperature.

Cremer found, further, that the same relation of a constant h was also fulfilled in a series of experiments by Grimm and Schwamberger.[390] These authors measured the reaction

$$C_2H_5Cl = C_2H_4 + HCl$$

at the surfaces of a number of univalent to quadrivalent chlorides. Their principal result is that, as in the case of Cremer, the activation energy increases with the ion distance. Cremer found that these researches, also, permitted arrangement into groups with constant h and Schwab found good agreement between the h values and the conditions employed in preparing the catalyst.

The experimental material is still scanty. The exponential relation between activity and activation seems, however, to be confirmed, contrary to the linear relation of Polanyi and Wigner.[391] Whether with sintered catalysts, the indicated relationship with the temperature at which exchange of positions last took place is a general one has yet to be tested. With practical contact masses, which are not systems in equilibrium, such a relationship is naturally not to be expected. At any rate we may be at least permitted to see, in the occurrence of this relationship, a support for our postulates concerning the energy distribution of the active centers.

More recently, Storch,[391a] in discussing the problem of the relation between activity and activation energy, rejects most of the evidence previously

[390] H. G. Grimm and E. Schwamberger, *Reunion Internat. Chim. Phys.*, p. 214, Paris (1928).

[391] M. Polanyi and E. Wigner, *Z. physik. Chem.*, A **139**, 439 (1928).

[391a] H. H. Storch, *J. Am. Chem. Soc.*, **57**, 1395 (1935).

discussed because he considers the examples cited are not simple reactions. He restricts his considerations mainly to the data of Palmer and Constable [339] on dehydrogenation of alcohols on copper and of Dohse [303] on the dehydration of these compounds at oxide surfaces. Storch concludes that the relationship cannot be due entirely to a probability distribution of active centers. He suggests that the frequency of energy exchange in the adsorbed phase may be reduced markedly when multiple adsorption occurs and hence be a function of the spacing of the catalyst atoms. He also discusses the possibility in reactions involving hydrogen of a quantum-mechanical "tunneling." He considers there is good evidence for the former effect. Fairclough and Hinshelwood [391b] have just extended this type of consideration to the functional relation between the constants of the Arrhenius equation for various homogeneous reactions. They have formulated a theory connecting the collision number–probability factor, ZP, and the activation energy, E, due to an assumed time interval between activation and reaction.

Recently, Roginsky and Rosenkiewitsch [344] have shown that their conception of reactions as a resonance effect between reactants and products requires a relationship of the same form for all, even homogeneous unimolecular, reactions. They therefore conclude that the case studied by Cremer is only a special case of their general rule and that the concept of active centers is not necessary. It remains to be seen whether the quantum mechanical effect actually obtains in heterogeneous catalysis and in what order of magnitude (see page 261): measurements can only be made at non-homogeneous surfaces which certainly display the distribution effect; up to the present the latter alone is adequate to account for the facts of adsorption and kinetics.

Physical Nature of the Active Centers: Attempts have not been wanting, in recent times, to develop, for the physical nature of the kinetically homogeneous active centers, more definite conceptions than were at first suggested in the original outline of Taylor or for the purposes of its statistical treatment. There is something alluring in the assumption that the active centers correspond to a stage in a discontinuous distribution, definable with reference to a model, rather than to regard them, as Frankenburger has done,[213] as a region taken from an energy continuum, in which intermediate stages of definite stability are realizable.

Three points of view may be mentioned in this connection. In the first place, the basic concept of active centers as "extra lattice atoms," atoms more or less free from the lattice, points to a discontinuous distribution.

[391b] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937).

The limited number of crystallographic directions in which a boundary atom of a crystal may be deprived of its neighbor, in other words, the necessary existence of surface, edge and corner atoms, yields necessarily a like number of energy steps, between which intermediate stages are presumably not possible throughout the entire region. One of these steps, possibly the energy richest, perhaps one which is spatially more favorable, may be regarded as active.

The actual existence of a lower limit for the activation energy is a second indication in the same direction. We have seen that it is this which makes the measurement of activation energies at all possible, and we have seen, further, that we can actually measure this limit approximately. It must correspond to the highest degree of unsaturation which is permissible with respect to the lattice in question and which, on the other hand, embodies a configuration capable of catalysis.

The third argument is the discovery of Dohse recorded in Fig. 36, according to which, in the catalytically active region, the distribution function is horizontal, involving atoms of like energy in finite numbers.

Some attempts to formulate such models will now be briefly discussed. Smekal[392] identifies the active centers with the " cracks " or imperfections in crystal structure, which, according to his theory of metallic conductivity break up the actual crystals into lattice units of approximately 10–100 atoms thick. It is from these cracks that, in an electrical field, especially energy-rich ions may be split off as conducting ions, and from which, also, photoelectrons are given up on illumination (inner photo-effect); in short, they are the specially reactive positions in the crystal, and, where they cut the surface, it is to be expected that especially active surface atoms will be found. The theory of loose ions at the Smekal cracks has recently encountered a series of difficulties, so that a definite decision in its regard is not yet possible. But the point of view that the active centers are crystallographically loosely bound units of structure naturally agrees well with other considerations in this regard.

Balandin, whose views have already been given [325] (page 251), has naturally to make his multiplet-hypothesis conform to the proved existence of active centers. He does this in this way. His multiplets, for example, the sextet involved in dehydrogenation (Fig. 32), are not parts of a complete lattice face but only nuclei of such, the first regular aggregation of the atoms, which are still distinguished by their large free valences, but are already regularly arranged.

A more general attempt to define the concept of active centers was under-

[392] A. Smekal, *Z. Elektrochem.*, **35**, 567 (1929).

taken by Schwab and Pietsch. Starting from a series of results, already mentioned, they arrived at the concept of active centers as " active lines." This concept was found to be in accord with the kinetics of the subject. Later [252] they cited a number of arguments from the energetic standpoint for such a postulate. Crystal edges, crystal boundaries and imperfections in the crystal should operate as active lines. The concept of the edges as the active centers conforms closely to that which we discussed previously concerning stepwise distribution: it describes an energetically preferred region of loosely bound structural units. A large number of examples show that this character also manifests itself in increased activity. Edges are the preferred centers of activity as nuclei of new crystals or even for the crystallization of other substances. They are the positions at which adsorption exchange occurs (exchange adlineation); they are the places at which chemical changes and the decomposition of crystals take place. Pietsch, Kotowsky and Berend,[393] by direct observation of macro-crystals, were able to show that any given reaction at a crystal-solution boundary begins, with perfect crystals, at the edges and then gradually extends over to the faces. As an example, the edges of copper sulphate pentahydrate become black in alcoholic hydrogen sulphide solution.

The same is true also for the boundaries of particles, which, in mixed catalysts, separate different components, but, in catalysts composed of one substance, separate different crystallites, regions which are crystallographically unequal. In the crystal boundaries, also, the atoms are bound to the neighboring lattice in a different manner, actually with weaker binding forces than they are to their own lattice. The great reactivity of the boundaries of particles is revealed by the more marked evaporation in this region, observed metallographically, and above all by the fact that all known reactions in which a solid phase results from another solid phase are localized in such zones of contact (see page 327). It is obvious that imperfections in lattice structure, whether they be the Smekal " cracks " or accidental mechanical imperfections, form active areas.[393a]

There is thus much experimental material indicative of the reactivity of active lines, less, however, for their consequent catalytic activity. So

[393] E. Pietsch, A. Kotowsky and G. Berend, *Z. Elektrochem.*, **35**, 582 (1929); *Z. physik. Chem.*, B **5**, 1 (1929).

[393a] It is perhaps worth recording that much of this evidence collected by Schwab and Pietsch concerning the activity of boundaries and interfaces was already cited and discussed by Taylor, *J. Franklin Institute*, July (1922) especially in its possible bearing on the problem of promoter action; such considerations, during the earlier work, are regarded by Taylor as contributory stages in the development of the general concept of active centers. Tr.

far as edges are concerned localization of catalysis at these, instead of on the whole surface, would require that the velocity be not proportional to the surface (or to the reciprocal diameter) but to its square. For, as can easily be shown, with like crystals of the same total mass, the sum of all the edges increases with the square of the surface. The experiments of O. Schmidt [316] previously cited, dealing with the ratio of activity to surface area, show a deviation from proportionality in this direction. Further experimental material by Schwab and Rudolph [393b] yields the same indication.

They repeated the experiments with a comparable series of preparations and find that the catalysis lies between the 1.8th and the fourth power of the surface. Their detailed discussion also shows that whole number exponents are not to be expected, but that an exponent greater than 1 compellingly demonstrates the activity of crystallographically exceptional elements of structure such as corners, edges, and the like. Schwab and Stauffer [252] have also observed catalysis by edges on macro-crystals. Examples of catalysis at crystal boundaries have already been cited previously, page 232; at imperfections in a surface, catalytic nuclei formation from solutions has long been known (scratching the walls to secure crystallization) and has also been observed with macro-crystals.

On the whole, this concept is closely allied with the more general concept of a rough surface in that the "mountains and valleys" of the latter are to be regarded as the microscopic edges and corners of the former.

This concept diminishes the force of the objection, raised by Schmidt [387d] against Taylor's theory, that the active atoms indicated in Fig. 35 must sinter much too fast to be catalytically active; for, in the sintering process, only crystals can result and, in these, corners and edges must occur in certain numbers. Further, there is an advantage in that the idea of unsaturation can thereby be expressed by lattice properties more susceptible to experimental investigation. This expectation has been fulfilled since, in the meantime, Kossel [394] has estimated electrostatically, by means of his theory of crystal growth, the energies of attachment of suitable lattice material at differently exposed positions of the lattice (active centers), and has shown that, actually,

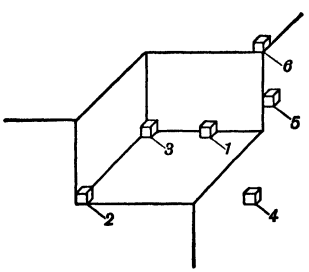


FIG. 37. Principal Points for the Addition of New Units to a Lattice (Stransky).

[393b] G.-M. Schwab and L. Rudolph, *Z. physik. Chem.*, B **12**, 427 (1931).

[394] W. Kossel, *Leipziger Vortrage*, page 1, 1928; *Naturwiss.*, **18**, 901 (1930).

a progressive decrease of unsaturation, in this sense, obtains. Stransky,[395] for example, gives for the positions indicated in Fig. 37 the following energies of attachment, in relative magnitudes, applicable to a regular ionic lattice:

(1) Inside Edge.....0.313 e^2/d.
(2) End of inside edge.....0.675 e^2/d.
(3) Inside corner.....0.807 e^2/d.
(4) Surface.....0.132 e^2/d.
(5) Edge.....0.181 e^2/d.
(6) Corner.....0.494 e^2/d.

d = lattice distance

This gain of energy on the attachment of lattice units may well be parallel to that obtained by the attachment of activated molecules and, hence, to the lowering of the activation energy. Stransky points out that, as compared with the edges, the corners have not hitherto been sufficiently taken into account, and that the latter must exert a catalysis proportional to the cube of the specific surface. There is no evidence of this and it is also possible that the corners, on account of their high adsorptive capacity, may remain continuously covered with reaction product. According to Herzfeld,[396] such relationships may be studied by means of the influence exercised on habit in crystal growth by substances present in the solution. Urea, for example, in a saturated solution of common salt, always occupies the corners of the cube so that these can no longer be active as nuclei for octahedral faces. As a result, the octahedral faces will be the slowest growing and, therefore, the final limiting faces.

In addition it has been pointed out by Stransky [396a] that, with respect to the crystal habit appearing on slow growth, there is a fundamental difference between heteropolar or ionic crystals on the one hand and homopolar crystals (to which the metals belong) on the other. In the latter, instead of corners and edges between the simple faces, there arise crystal surfaces of higher indices, which suppress the edges and corners. Since these are the surfaces of highest specific energy they are probably to be regarded as the positions of the active centers. These surfaces have only small surface area, corresponding to their high surface energy; they operate

[395] I. N. Stransky, *Z. Elektrochem.*, **36**, 25 (1930).

[396] K. F. Herzfeld, *Colloid Symp. Ann.*, page 51 (1930).

[396a] I. Stransky, *Z. physik. Chem.*, B **11**, 342 (1931); *Z. Kristallogr.*, **78**, 373 (1931); **88**, 325 (1934).

therefore geometrically like edges and corners and thus account for the observations of Schwab and Rudolph.[393b]

The preceding data on crystal growth were compiled with reference to ionic lattices. Quantum-mechanical studies [396b] on the crystal growth of metal lattices from metal vapors indicate quite definitely that the basic ideas in Taylor's original theory of active centers [280, 281] as to the nature of unsintered unstable active catalysts are essentially correct. It appears that a small group of atoms tend to arrange themselves in non-symmetrical arrays such as linear sequences or filaments of atoms and that atoms attach themselves readily to corners of the lattice, projecting outwards into space. It emerges also that the change from such unstable non-lattice arrangements to the ordered array of the normal crystal lattice is attended by a quite marked activation energy, which agrees qualitatively, at least, with the observed progressive increase of sintering as such unstable systems are subjected to progressively higher temperatures, in itself an experimental evidence of definite activation energies in such processes.

The newer additions to the theory of crystal growth have at least shown that the attempt to identify the active centers as atoms of a homogeneous, definite, crystalline type obtains full confirmation and quantitative bases from this source so that a further pursuit of the work appears full of promise.

In this connection we may refer to the studies of Pietsch and his collaborators,[396c] even though they have been, in certain details, carried somewhat far. They have attempted to treat the phenomena of corrosion and solution of metals from the standpoint of active lines.

Interesting investigations on how the catalytic activity, and therefore the number and kind of centers, change when phase changes occur have been carried out by Hedvall. It was shown in numerous cases that sharp maxima of solution velocity and chemical reactivity occur at transition points, and at changes in secondary structure (*e.g.*, Bi at 75° C.), as well as at the Curie point and its electrical analog. Then, it was presumed that catalysis would show a similar behavior at such transition points. It was demonstrated experimentally that a sharp development of nitrous oxide decomposition on nickel set in at the Curie point, a discontinuous change of the direction of reaction between carbon monoxide and hydrogen, as well as an acceleration of the reaction $2CO = CO_2 + C$ at the surface

[396b] H. S. Taylor, H. Eyring and A. Sherman, *J. Chem. Phys.*, **1**, 68 (1933).

[396c] E. Pietsch and E. Josephy, *Z. Elektrochem.*, **37**, 823 (1931); E. Pietsch, B. Grosse-Eggebrecht and W. Roman, *Z. physik. Chem.*, A **157**, 363 (1931); E. Pietsch and E. Josephy, *Korrosion u. Metallschutz*, **8**, 57 (1932).

of a nickel-copper alloy at the Curie point.[396d] It is unfortunately to be recorded that the catalysts studied react in every case with the substrate, so that the interesting findings should be remembered but are not yet entirely compelling.

Another concept concerning the nature of the active centers results from the analysis by Sherman and Eyring [396e] of the activation energy of activated adsorption of hydrogen by charcoal. They show that a quantum mechanical analysis of this process indicates that a most favorable carbon-carbon atom distance exists (at approximately 3.6 Å.) such that the activation energy of adsorption is a minimum. An extension of this view to catalytic processes would suggest that it is particular geometric configurations of atoms which form the active centers of a catalyst surface, and that these are effective by reason of the low activation energies obtaining at such centers for the activated adsorption which is a necessary preliminary to the catalytic reaction.

[396d] Hedvall and Schiller, *Z. anorg. Chem.*, **221**, 97 (1934); Hedvall, *Svensk. Kemisk. Tidskr.*, **45**, 80 (1933); Hedvall and Gustavson, *ibid.*, March (1934); Hedvall, Hedin and Ljungkvist, *Z. Elektrochem.*, **40**, 300 (1934); Hedvall, Floberg and Palsson, *Z. physik. Chem.*, A **169**, 75 (1934); Hedvall, Hedin and Persson, *Z. physik. Chem.*, B **27**, 196 (1934); Hedvall, *Chem. Rev.*, **15**, 139 (1934); Hedvall, *Z. Elektrochem.*, **41**, 445 (1935); Hedvall and Pauly, *Z. physik. Chem.*, B **29**, 225 (1935); Hedvall and Afzelius, *Svensk. Kemisk. Tidskr.*, **47**, 156, 161 (1935).

[396e] A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

CHAPTER XVI

MIXED CATALYSTS, SUPPORTED CATALYSTS AND PROMOTER ACTION

HITHERTO the discussion has been limited, at least as far as fundamentals are concerned, to catalysts the material of which was chemically uniform. The possibilities of heterogeneous catalysis are multiplied if catalysts are prepared with several components. There are, obviously, many possibilities, such as mechanical mixtures, chemical compounds, mixed crystals, surface compounds between the components of the catalyst and all intermediate stages of these same. In this connection a difficulty of definition arises: shall a chemical compound of two elements such as Al_2O_3 be considered as a mixed catalyst? This question far transcends the mere problem of definition because such a concept under certain circumstances may contain in itself a physical interpretation of certain phenomena. We shall, therefore, raise this question at the very outset.

It will be recalled that the phenomena of selective catalysis and their variation by pre-treatment of the catalyst have led us to the conclusion that a contact mass, such as glass in the decomposition of formic acid, or zinc oxide in the decomposition of alcohol, consists of at least two different regions or, as we may now say, two types of active center.

May it not be that the one kind consists of zinc ions, the other of oxygen ions. This theory was also put forward by Taylor.[274] He assumes that on oxide latticcs, which both dehydrogenate and dehydrate alcohols, the metal ions effect the dehydrogenation, as in metals, and the oxide ions the elimination of water. As a result, the dependence of the ratio of the two reactions on subtle conditions of preparation, contact with the preparative solutions, etc., is easily understandable since the ratio of the two ionic constituents of the lattice in the free surface can be subjected to considerable variation of recrystallization, adsorption or poisoning. For example, Taylor shows that tungsten oxide which, in the reduced state, strongly dehydrogenates, is in the oxidized condition strongly dehydrating.

Other findings, however, are opposed to this point of view. Thus, by adsorption of anions, metal ions must, in general, be poisoned and hydrogen production fall; by adsorption of cations on the oxide ions, on the other

hand, ethylene formation should be retarded. Adkins and Millington [359] find, on the contrary, that an effect in the first direction only is obtained, irrespective of whether their zinc oxide was treated with sodium hydroxide or sulphuric acid. Also, the influence of a given addition for different alcohols is different; the relations are therefore much more complicated and the chemical definition of active centers as ions of different signs does not yet seem to be certain.[396f]

Definition of Mixed Catalysts: In the following paragraphs, therefore, we shall not include chemical compounds of the usual type and shall understand as " mixed catalysts " those systems defined by Mittasch [347] thus: " A mixed catalyst is one composed of two or more constituents or substances so incorporated that the ratio of the amounts of these constituents obtaining during catalysis, is arbitrarily determinable, within certain limits, in the preparation of the catalyst." Not only are all stable compounds thus excluded from the concept of mixed catalysts but also all kinds of intermediate compounds formed in the process of catalysis, such as palladium hydride or platinum oxide.[397] The latter perhaps should not be unconditionally excluded. Willstätter [10] finds in the stimulating action which oxygen exercises on hydrogenation by platinum, a typical case of mixed catalysis such as we shall immediately learn to recognize. There are, however, other interpretations of this phenomenon, such as that due to Kuhn,[398] that oxygen retards the recombination of nascent hydrogen on platinum, and especially that due to Bodenstein,[324] according to which oxygen acts as a remover of a poison. The oxygen treatment dehydrogenates, to the metallic condition, the inactive catalyst which results,

[396f] In respect to this theory of dual surfaces, it seems necessary to emphasize that the conclusions reached as to the characteristics of such surfaces have hitherto been based on an entirely too restricted range of experimental measurements. A multiplication of such measurements by Taylor and Sickman, *J. Am. Chem. Soc.*, **54**, 602 (1932) served to show definitely that, for even approximately reproducible results, the most stringent regulation of a variety of experimental details must be arranged. These authors found a tenacious adsorption of water by zinc oxide to be an important factor in the velocity of decomposition of alcohols. Additional data on ratios of dehydrogenation to dehydration on the oxide and salts of manganese were obtained by A. T. Williamson and H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 3270 (1931) which indicate the strong dehydration action in presence of tervalent and quadrivalent anions. A discussion of this subject from the standpoint of velocity of activated adsorption and desorption of hydrogen and water vapor on the various oxide catalysts has been given by Taylor, *Z. physik. Chem.*, Bodenstein Festband, page 475 (1931), and by Taylor and A. J. Gould, *J. Am. Chem. Soc.*, **56**, 1685 (1934).

[397] de la Rive, *Ann. Physique*, **46**, 189 (1834).

[398] R. Kuhn, *Naturwiss.*, **13**, 169 (1925).

according to Bredig and Allolio,[399] from the formation of inactive platinum hydride. The question, whether we are dealing here with a typical case of mixed catalysis is not, however, settled by reason of these other possible modes of interpretation, since a variety of other such "stimulating actions" [399a] are known in which oxygen, hydrogen, carbon monoxide or carbon dioxide, in traces, accelerate heterogeneous reactions.

In this connection, the influence of gas treatment on the para-hydrogen conversion on charcoal [334b] and on the photoelectric effect on platinum [399b] may be noted and are perhaps definitive. The same is true of the so-called "weak spot effect" of Hüttig,[399c] a term which signifies that a catalyst is especially suitable for catalytic reactions of that substrate that has been present in its preparation. This is explained on the basis that places which preferentially adsorb the substrate in question have already been stabilized by adsorption during the preparation.

Promoter Action: If now we consider the genuine cases of mixed catalysts our interest at once centers in the widespread phenomenon that the two or more constituents do not show a simple additivity of their separate efficiencies for a given reaction but that the mixture can exert, not only a more powerful action than the individual constituents, but may also exercise new functions. We are here dealing with a special phenomenon requiring a special definition. According to Pease and Taylor [400] it comprises "cases in which a mixture of two or more substances are capable of exerting a greater catalytic activity than one would expect on the assumption that each substance in the mixture acts independently and proportional to its amount present." For this phenomenon, different designations have been proposed. The original German patents of the "Badische Anilin und Soda-Fabrik" in which Mittasch first recorded his experience in this subject, designated the phenomenon as "Aktivatoreffekt" because the substance added, which "activates" a catalyst to a new or stronger action, was termed as "activator." The corresponding documents in the English language introduced the term "promotor" or "promoter." This expression is quite general today in the English scientific literature.

Promoter action was discovered as Mittasch was searching for suitable technical catalysts for the Haber-Bosch synthesis. He observed [347] that ni-

[399] G. Bredig and R. Allolio, *Z. physik. Chem.*, **126**, 41 (1927).
[399a] G.-M. Schwab, *Erg. exakt. Naturwiss.*, **7**, 331 (1928).
[399b] E. Schaaff, *Z. physik. Chem.*, B **26**, 413 (1934).
[399c] O. Kostelitz and G. F. Hüttig, *Koll. Z.*, **67**, 265 (1934).
[400] R. N. Pease and H. S. Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

tride formation by silicon was improved by the presence of alkali and the possibility that the same might be true in the case of ammonia formation led him to test systematically a large number of additions to metals.[401]

Examples of Promoter Action: Quite generally, it was shown that metals such as iron, molybdenum and tungsten, nickel and cobalt were promoted for ammonia synthesis by difficultly fusible and difficultly reducible oxides such as alumina, magnesia, the rare earths, chromium oxide and manganous oxide. The classical contact mass in ammonia synthesis consists of iron containing much alumina and some potash. Low melting metals such as lead act as poisons, as do sulphur compounds. Many additions, such as boron and carbon, are quite indifferent, that is to say, their action is additive and the total activity corresponds to that of the iron content. The metals can also promote each other (mutual promotion). The following mixtures have been recognized as ammonia catalysts:

FeMo	NiMo	CoMo	PdMo
FeW	NiW	CoW	PdW
FeLi	NiLi	CoLi	PtMo
FeSr	NiCa	CoNa	PtW

Even metals which are each separately inactive can give good ammonia yields when mixed, for example, AlMg or CrZn or ternary mixtures such as AlCrNa, MoPdK, $MoPdUO_2$, the " formulae " revealing nothing, however, of the ratios of the constituents present.

In hydrogenation, similar effects are possible; for example, nickel is promoted by alumina. In Germany, the Ostwald process of ammonia oxidation on expensive platinum was replaced by the cheaper mixture of $Bi_2O_3-Fe_2O_3$. Contact masses for the methanol reaction have already been mentioned (page 264) and the possibilities of different reaction paths by modification of the catalyst. " Hopcalite " is a mixture which also belongs in the present category, consisting, in its simplest form, of a mixture of copper oxide and manganese dioxide, permitting the selective combustion of carbon monoxide to carbon dioxide in mixtures with hydrogen.

The types and range of promoter action are quite varied. Mittasch[402] gives, in this connection, a very instructive diagram, Fig. 38, which will serve for purposes of classification. When the line indicating the different activities (yields, or better still, velocity constants) as a function of com-

[401] A still earlier patent to Schering (D. R. P. 219043/44, 1908; B. P. 19249, 1910) decisively demonstrates the beneficial action, catalytically, in hydrogenation reactions, of small additions of foreign substances, such as alkali, to the catalyst preparation. Tr.

[402] A. Mittasch, *Ber.*, **59**, 13 (1926).

position is a straight line, we speak of additivity or absence of promoter action as, for example, in the case of boron or carbon with iron catalysts in ammonia synthesis, studied by Mittasch,[347] and also in the case of zinc and magnesium oxides in the decomposition of nitrous oxide investigated by Schwab and Schultes.[332] When the curve is convex to the composition axis we have cases of poisoning. In ammonia synthesis, according to Mittasch and Frankenburger,[403] the elements S, Se, Te, As, P, Pb and Bi behave thus towards metal catalysts. Chromium oxide acts thus towards other oxides in the decomposition of nitrous oxide.[332] Thallium in lead retards the recombination of hydrogen atoms.[403a] If the activity of the mixture only increases slightly over that of the pure component B and if, also, the activity remains substantially constant, even on great dilution with A (dotted line in the diagram), we speak of carrier action and designate the substance A as a catalyst support. To this category belong the well-known contact masses composed of platinum, palladium or copper carried on asbestos, pumice, porous porcelain and barium sulphate, also nickel on alumina or kieselguhr, and lead promoted by potassium chloride.[403a] If the curve rises markedly above the connecting line, there are two cases to be differentiated: simple promotion, when the component A alone is inactive, and coactivation when both components act catalytically. There are many examples of such in the systems cited.

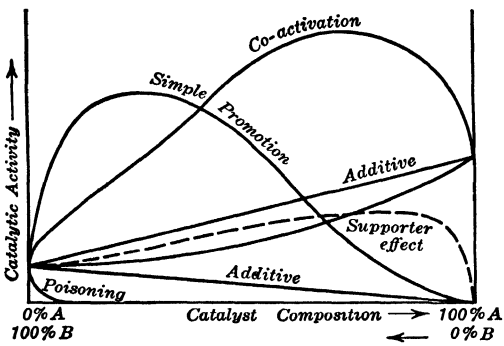


FIG. 38. Activity of Mixed Catalysts (Mittasch).

In catalysis by colloidal catalysts in solution there are, in addition, " protected catalysts " containing a protective colloid. The function of the latter is analogous to that of a support; we shall consider this group separately (page 333) as well as mixed enzymes.

Causes of Promoter Action: The causes of this important phenomenon of promoter action are in no way the same in all systems, and it is not possible to say with certainty, even for a single special case, that there is only one mechanism of promotion. Even in the first publications on this subject, the

[403] A. Mittasch and W. Frankenburger, *Z. Elektrochem.*, **35**, 920 (1929).

[403a] E. Pietsch and F. Seuferling, *Z. Elektrochem.*, **37**, 655 (1931); *Z. physik. Chem.* Bodenstein Festband, 523 (1931).

patent literature, Mittasch and his collaborators noted the multiplicity of possibilities, part chemical and part physical.

It must first be pointed out that, as we saw previously, a catalyst is more active the more finely divided it is. This makes probable the opinion expressed even by the discoverers of the phenomenon that an added foreign body would prevent the growth of the individual crystals, during the preparation or in course of use, to form larger crystals, so that the promoted product has simply a large surface. The observations of Baxter [404] support this point of view. He showed that gas adsorption by metals which were not pure was greater than that by metals of atomic weight purity. The promotion of nickel for hydrogenation purposes by a variety of materials is attributed to this action by Armstrong and Hilditch.[405] This explanation cannot be entirely adequate since Mittasch[347] has observed that, in this case, there are also directive influences of the promoter in various alternative reactions. The mere extension of surface would imply a simple carrier action. Such catalysts would also be relatively stable to heat, as Bray and Doss [406] find for hopcalite.

X-rays and Promoter Action: Decisive proof of this effect is obtained from X-ray investigations, first by Wyckoff and Crittenden[384] and later by Brill.[406a] Wyckoff and Crittenden demonstrated that in the oxide mixture used for the formation of the $Fe-Al_2O_3-K_2O$ catalyst for ammonia synthesis, the Fe_3O_4 yields its excess of FeO to the promoter $2Al_2O_3 : 1K_2O$, which forms therewith a homogeneous compound, a spinel, as shown by the disappearance of the FeO lattice. On subsequent reduction of this homogeneous phase, iron results in an extreme state of division as recognized by the breadth and diffuseness of the interference lines. Furthermore, the promoter prevents the iron particles growing to larger aggregates when the prepared contact mass is subjected to heat.

These X-ray discoveries were confirmed by investigations of Frankenburger and Mayrhofer [335] based upon this concept. Whereas pure iron, condensed from its vapor, is able to fix only small amounts of hydrogen and no nitrogen, hydrogen adsorption, in particular, immediately increases markedly with iron distilled on to a wall simultaneously with a foreign body acting as a promoter. Ice and sodium chloride were chosen as the materials to be deposited with the iron. These " model " catalysts are also more heat

[404] G. P. Baxter, *Am. Chem. J.*, **22**, 351 (1899). The significance of this work as one explanation of the subsequently discovered phenomenon of promoter action was first emphasized by Rideal and Taylor, Catalysis in Theory and Practice. 2nd. Ed. Tr.

[405] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.*, A **103**, 586 (1923).

[406] W. C. Bray and G. J. Doss, *J. Am. Chem. Soc.*, **48**, 2060 (1926).

[406a] R. Brill, *Z. Elektrochem.*, **38**, 669 (1932).

resistant than pure iron for they show recrystallization, with re-emission of adsorbed hydrogen, at higher temperatures than pure iron. With ice, the recrystallization occurs at $-150°$ C., with common salt at $+30°$ C.

Activity Distribution in Promoted Catalysts: Nevertheless, similar conditions obtain in the case of promoted catalysts as are found elsewhere: not only the extent, but also the activity of the surface, that is to say the content of active centers, is increased by promoters. W. W. Russell and Taylor [407] demonstrated that the increase of adsorption was only about one fifth part of the reaction acceleration.

A research of Almquist and Black [367] contains perhaps even more penetrating conclusions. We recall that the interpretation of the poisoning of iron by oxygen as due to compound formation could be regarded as supported by the fact that catalysis ceased when the ratio of steam to hydrogen in the gas corresponded to that at which thermodynamically the gas mixture could just oxidize iron. The authors mentioned have performed analogous experiments with promoted iron, namely, with a technical synthetic ammonia contact mass. It was shown, thereby, that much smaller water vapor pressures sufficed to oxidize the finely divided iron, that is, to poison it. The diminution in the critical relation $H_2O : H_2$ is directly connected with a diminution in the heat of the reaction, that is to say, with an excess energy of the active centers. Calculation showed this excess energy to be many kilocalories. Direct measurements of heats of adsorption on promoted catalysts by Fryling [268] show an increase in these heats for similar extent of adsorption, and hence an increase in the active fraction of the total surface.

Schenck and Wesselkock [408] have further developed this method of quantitatively characterizing promoter action by means of the composition of the equilibrium gas mixture. As a measure of the excess energy they employed the reaction

$$CO_2 + Me \rightleftarrows CO + MeO,$$

in other words, they measured the content of the gas phase in carbon dioxide, which still first causes oxygen to be taken up by the condensed phase. From the equilibrium

$$2CO + O_2 = 2CO_2$$

the oxygen pressure corresponding is given by the expression

$$[O_2] = \frac{K\,[CO_2]^2}{[CO]^2}\,.$$

[407] W. W. Russell and H. S. Taylor, *J. Phys. Chem.*, **29**, 1325 (1925).
[408] R. Schenck and H. Wesselkock, *Z. anorg. allgem. Chem.*, **184**, 39 (1929).

It emerges that iron, cobalt and nickel are promoted as regards their oxidation by all the oxides such as CaO, MgO, MnO which possess the same sodium chloride lattice and lattice constants similar to those of FeO, CoO and NiO. These oxides are promoted, therefore, by such oxides as can form homogeneous phases or mixed crystals with them. The promotion is greater, the nearer the lattice constant of oxide and promotor lie to one another, with only one exception. Also, aluminum oxide, which does not indeed form mixed crystals but does form a homogeneous compound, a spinel, operates in the same sense. Ternary mixtures such as CoO, Al_2O_3, MgO act still better. Whereas, at 900° C., in contact with pure cobalt, 95 per cent carbon dioxide is required for oxidation, with the mixture cited 7.5 per cent suffices. From these data one can calculate an excess energy, E, from the expression

$$e^{\frac{E}{1173R}} = \left(\frac{95}{5}\right)^2 : \left(\frac{7.5}{92.5}\right)^2 = 55{,}000$$

whence E amounts to the very considerable value of 22 kilocals. The cobalt particles reduced from the homogeneous phase, mixed crystal or spinel therefore possess an increased heat of combustion equal to this figure.[408a]

According to Schenck, the increased energy yield on oxidation is a result of the formation of a homogeneous phase, a kind of heat of solution, therefore. The decomposition of methane to yield carbon, in which no oxide results, should, therefore, not be promoted. Since, on the other hand, quite analogous systems are good, promoted ammonia catalysts, which, according to Schenck's view would not be expected, it remains an open question whether the excess energy would not be found with other processes than that of oxidation, for example, with activated adsorption, whether, therefore, it does not arise by reason of a state of division, one especially rich in edges and corners.

Structural Promotion: In any case, by reason of these investigations, a fruitful path for the measurement of energy has been explored and the fact demonstrated that a promotion exists which consists in the increase and maintenance of energy rich centers. We shall designate such cases as " physical " or " structural " promotion, and the effect of stabilization against overheating as " prevention of sintering."

[408a] It is perhaps worth pointing out here that this method of studying the equilibrium position was early utilized by Richardson, Vibrans and Bell, *Science*, **56**, 27 (1922), and by Pease and Cook, *J. Am. Chem. Soc.*, **48**, 1199 (1926) with reduced iron and nickel respectively, and with the oxides produced by reaction of the metals with steam, to indicate the presence of centers of excess energy even in unpromoted materials. Tr.

Phase Boundaries and Promoter Action: Besides this mechanism there are, however, others possible, in which it is not the state of division of a component which confers the superiority but, for other reasons, the phase boundaries, necessarily present in the surface of the mixture, are the topochemical requirement for, and location of, an increased reaction velocity. Thus, Cassel,[409] and, prior to him, K. A. Hoffmann,[410] point out that the following mechanism suggests itself: the one component of the catalyst may adsorb practically only the one, the other component essentially only the other reactant. Then the two participants in the reaction can only come together at the phase boundaries in sufficient concentration and in a sufficiently activated, adsorbed condition, whilst each component alone is not a good catalyst. Two-dimensional diffusion on the surface (page 188) facilitates such effects.[410a]

It is possible that, sometimes, the one component accelerates the intermediary reaction of the substrate with the other and vice versa, which again is only possible at the phase boundary. How this is to be understood follows from the remarkable findings of B. Neumann.[278] We have already seen that catalysis by oxides in the contact sulphuric acid process can be conceived as an alternate oxidation and reduction of the catalyst. If now, the reduction of the catalyst by sulphur dioxide is the slowest process, additions to the mass capable of effecting rapid reduction will bring about promotion. Thus, the difficultly reducible oxides, Fe_2O_3 and Cr_2O_3 will be promoted by SnO_2 since the intermediate SnO is a strong reducing agent. If, however, the re-oxidation of the contact agent by oxygen determines the velocity, rapidly oxidizing addition agents will act as accelerants. Thus, vanadium pentoxide which is not too rapidly re-formed from the intermediate stage, V_2O_4, is promoted in its activity by silver, since the intermediate silver oxide, Ag_2O, is a strong oxidizing agent.

If this view of the condition of affairs is correct, iron oxide cannot be promoted by silver nor can vanadic acid be promoted by stannic oxide, since silver is not a strong reducing agent nor is stannic oxide a remarkable oxidation agent. This is actually the precise state of affairs. Promotion arises in these cases by reason of a reaction of the phases of the catalyst with one another, a reaction naturally restricted to the phase boundaries. We can designate this as " chemical promotion " without undue restriction being placed on this expression.

[409] H. Cassel, *Naturwiss.*, **14**, 103 (1926).

[410] K. A. Hoffmann, *Ber.*, **49**, 2369 (1915).

[410a] Such a mechanism for mixed catalysts is suggested by the original patent literature on ammonia synthesis and was specifically formulated by Rideal and Taylor, " Catalysis in Theory and Practice," page 31, 1st Ed., Macmillan and Co., London, 1919.

It may also be noted that the influence of a second substance on the reaction of a constituent of a contact mass is, of course, not always a promoting effect. Neumann, Kröger and Iwanowsky [410b] have found cases in the oxidation of carbon monoxide, where poisoning and promotion alternate in the same pair of catalyst constituents, depending on the composition and the temperature.

A simpler example obtains in the case of hopcalite, in which, according to Hoskins and Bray,[411] the two oxides accelerate each other's reduction by carbon monoxide. Naturally, too, all these cases belong to the group of reactions discussed on page 231 in which gas reactions of oxygen and especially the hydrogen-oxygen reaction take place at the boundary, metal-metal oxide, as, for example, in the case of the hydrogen-oxygen reaction at copper, which has been elucidated especially by Pease and Taylor [411a] and by Okayama [341] in addition to the authors previously cited. The reaction at the phase boundary consists in the transition, there, of the metal to oxide and vice versa, and hence the successive reactions

$$2Cu + O_2 = 2CuO$$
$$2H_2 + 2CuO = 2H_2O + 2Cu.$$

Hinshelwood [12] declares it to be desirable that more investigations of promoter action should be made with reactions having only a single reactant gas, in order to separate the boundary effect already mentioned from any "real" promoter action. We shall return later to this proposal (page 307). It implies that, besides the possibilities already discussed, there is still a possibility of another type of activity of the boundary lines.

This point of view has also been expressed from many different quarters. Balandin [325] concludes from his multiplet-hypothesis that, at phase boundaries, doublets of a new type arise, one center of which belongs to one, the other to the second constituent of a mixed catalyst. In a quite similar manner, Burk makes the activity of the phase boundary plausible. It is known that the decomposition of ammonia at platinum surfaces is retarded by hydrogen (page 225); from his own investigations Burk concluded [412] that, on molybdenum surfaces, nitrogen exerts a retarding effect.[413] If, now, platinum adsorbs hydrogen predominantly and molybdenum nitrogen, at a phase boundary of a Pt—Mo mixture we should have an "adlineated"

[410b] B. Neumann, C. Kröger, and R. Iwanowsky, *Z. Elektrochem.*, **37**, 121 (1931).

[411] W. M. Hoskins and W. C. Bray, *J. Am. Chem. Soc.*, **48**, 1454 (1926).

[411a] R. N. Pease and H. S. Taylor, *J. Am. Chem. Soc.*, **43**, 2179 (1921); **44**, 1635 (1922).

[412] R. E. Burk, *Proc. Nat. Acad. Sci.*, **13**, 67 (1927).

[413] See, however, C. Kunsman, *J. Am. Chem. Soc.*, **50**, 2100 (1927). The affinity of molybdenum for nitrogen is nevertheless well known.

ammonia molecule with the hydrogen atoms drawn to the platinum side and the nitrogen to the molybdenum side; there should be an easier decomposition of the molecule through such a multiple adsorption. In actual fact Burk found, with such mixtures, an enhanced reaction velocity and an activation energy lower than those obtaining with the single components (the data are given on page 238).

Synergetic or Co-operative Promotion: We shall now consider a reason for the activity of phase boundaries which is of another and more fundamental nature than the localization determined by adsorption, transport or chemical processes, and that is " the quite specific arrangement of the field of forces at such places." Willstätter [1] especially has voiced this point of view with great emphasis by pointing out that " mixtures can have the properties of new chemical compounds," in that the atomic fields of the components overlap each other and alter one another. He designates this process of specific mutual action as " synergy " and defines it thus: " that, in mixtures of substances, the physical and chemical properties of a single component may suffer important changes through the influence of one or more other components." [10]

His numerous experiences in the field of mutual promotion by enzymes (see page 340) formed the starting point for Willstätter. But physicochemical theory of catalysis would also suggest such effects. Haber [342] has pointed out that, at the places of contact of different substances, the new fields of force which arise also induce new types of moments in the adsorbed molecules and can thereby lead to promoter action. Mittasch [347] has also mentioned such a possibility. Thus, he points out that the promotion of osmium by alkali cannot be of a purely structural nature since even pure osmium shows no sintering. The mixed catalyst nickel-molybdenum, in which, according to an investigation of Kuss and Keunecke,[414] the compound NiMo is the catalyst and nickel is the promoter, also has characteristics which are not explainable by structural promotion. Starting from a consideration of the localization of catalytic action which is chemically determined and which, in the final analysis, owing to the real identity between intermediate compound and adsorption complex, can also be regarded as specific " synergy," or " co-operation." Schwab and Pietsch [252] have especially emphasized the exceptional fields of force at the boundaries of particles. Such boundary lines are, naturally, also capable of producing greater directive effects on a reaction sequence than are possible with single contact masses, by reason of the occurrence of non-additive resonance relations in the sense of London's theory.

[414] A. Kuss and E. Keunecke, *Z. Elektrochem.*, **36**, 690 (1930).

The asymmetrically operating mixed catalysts studied by Schwab, Rudolph and Rost [363c] show this definitely. In these studies, the copper, which is quite non-specific from the asymmetric point of view, is so influenced by the optical asymmetry of the quartz which is acting as support that optically specific catalysis ensues at the phase boundaries. It will be advantageous to designate such effects as " synergetic " or " co-operative " promotion. With most mixed catalysts they will play a definite rôle and with some the most important rôle.

Differentiation of Structural and Synergetic Promotion: The question may now be asked whether there exists a characteristic with the help of which structural and synergetic promotion may be distinguished from one another, without assuming, however, that this differentiation covers all possible promoter effects. Schwab and Schultes [332] have attempted this in a simple example. They chose for this the reaction of a single substance because, in such case, a series of alternative possibilities is eliminated. The reaction chosen was the decomposition of nitrous oxide

$$2N_2O = 2N_2 + O_2.$$

Copper oxide, from 300° C. upwards, is a good catalyst for this reaction. A preliminary ignition diminishes its activity because the number of active centers is smaller, due to sintering. Their nature and position, however, remain the same, as is evident from the constancy of the activation energy, which amounts to 24 kilocals. In ignited mixtures, with zinc oxide and with magnesium oxide, the activity of the copper oxide is enhanced over and above that due to additivity. In the zinc mixture, however, the velocity varies as a function of the composition in such a way that the additivity relation shown by the straight line in Fig. 38 is exceeded when the comparison is made with ignited copper oxide. The additivity relation holds, however, when the comparison is made with the more active, unignited copper oxide. By ignition in the mixture the activity of the copper oxide has not been reduced. Zinc oxide prevents sintering; it promotes structurally.

With additions of magnesium oxide it is otherwise. The additivity relation is here much more markedly exceeded so that the content of unignited copper oxide does not account for the observed velocity. One must therefore conclude that some type of influence other than that of prevention of sintering is present, that synergy obtains.

The means whereby such a conclusion is rendered certain is the observation of the temperature coefficient, the activation energy. Since the activation energy on copper oxide is not dependent on the degree of sintering, structural promotion should not alter it either. Actually, with zinc oxide

admixture of chromic oxide on both the velocity and extent of adsorption is undoubtedly of fundamental importance in the field of promoter action, the velocity factor being of primary importance in the case of technical processes involving streaming gases. References to other work of this type have already been given (page 208).

Promoter Action in Alternative and Successive Reactions: Hitherto, we have limited ourselves in principle to promoter action in simple reaction and have already stated that all the possibilities of a more than additive effect have not been exhausted. As soon as the reaction is divided into partial, simultaneous or consecutive reactions, there is still the further possibility, according to Medsforth,[416] that one of the components of a mixed catalyst accelerates one of the necessary successive reactions, which the other cannot influence. Such processes, which occur via gaseous or dissolved intermediate and separable stages, are naturally also not restricted to the areas of contact of the components.

Medsforth is of the opinion that the reduction of carbon monoxide and dioxide to methane and unsaturated hydrocarbons only occurs on promoted nickel because nickel alone catalyzes only the partial reaction

$$CO + 2H_2 = CH_3OH$$

and not the succeeding reaction

$$CH_3OH = H_2O + >CH_2$$

which, however, as is well known, occurs at oxide surfaces.[303] Argument against this interpretation can, however, be definitely raised. But, as we have already noted, by the combination of suitable catalysts, selected for their different efficiencies in the various reactions of the methanol scheme (page 264), directive effects of a very specific nature can be secured.

Another reaction, offering a similar possibility of solution, is the oxidation of ammonia. The contact mass suitable for this process, $Fe_2O_3-Bi_2O_3$, operates additively, according to recent investigations,[347] and yet is promoted as compared with the components so far as yield is concerned. This may be explained on the basis that the different selectivities of both components involved different initial temperatures and different temperatures of optimum yield, so that, by additive superposition, no partial reaction is accelerated but the region of high yields is broadened.

We have already learned of cases in which the two catalysts separately accelerate successive processes, even in homogeneous systems, for example, in the case of the copper-iron couple (page 84). They are also of impor-

[416] S. Medsforth, *J. Chem. Soc.*, 113, 1452 (1923).

tance in heterogeneous catalysis more especially on account of their applicability in industry. The possibility that the promoter or support may serve as an acceptor for a poison or retarding reaction product,[417] has also been made use of in practice.

At this point some important results may be mentioned which follow from studies by Hüttig and his collaborators concerning the formation of mixed catalysts from two solid components.[417a] These investigators conclude that compound formation in binary solid systems occurs through unstable intermediate states, which, by an abnormality of different properties, for example, the magnetic susceptibility, can be recognized during the heating period. During the interval of maximum appearance of such an unstable intermediate, the catalytic activity generally shows a maximum, depending partly on the lowering of activation energy on the new centers and partly on the great number of these centers.

At this stage the field of mixed catalysis may be left. We have seen that, in general, it may be treated adequately with the concepts of catalysis already at our disposal and that, in its turn, it has yielded contributions to these concepts. It must not, however, be overlooked that there still remains much to be done corresponding to the many possibilities of combining mixtures and reaction types, and that therefore our discussion of one series of possibilities is but one theory of mixed catalysts.

[417] K. W. Rosenmund, *Ber.*, **56**, 2262 (1923); *Z. angew. Chem.*, **38**, 145 (1925).

[417a] See, for example, G. F. Hüttig, H. Tschakert and Kittel, *Z. anorg. Chem.*, **223**, 241 (1935); Hüttig, *Z. Elektrochem.*, **41**, 527 (1935); Th. Meyer and Hüttig, *Z. Elektrochem.*, **41**, 429 (1935); Hüttig, Novak-Schreiber and Kittel, *Z. physik. Chem.*, A **171**, 83 (1934).

CHAPTER XVII

HETEROGENEOUS CHAIN REACTIONS

We have already seen in our discussion of homogeneous gaseous catalysis how profound may be the effects of a catalyst if it causes the termination of a spontaneously occurring chain reaction. The question arises whether, in addition, through heterogeneous catalysis, the initiation of a chain can be caused. This question was first propounded only a short time ago when the knowledge of chain reactions, and that of heterogeneous reactions, had so far developed that one could postulate that reactions in which an energy-rich intermediate, capable of functioning as a link in a chain, might ensue at suitable catalyst surfaces through deformation or loss of energy in triple collisions.

It must further be postulated that the resulting chain-propagating product shall be able to get away from the surface into the gas phase. The energy liberated by the primary surface reaction must bring the chain producer out of the surface to be used in the gas phase for starting the secondary chain processes. Is such a production of energy-rich bodies in heterogeneous reactions and their evaporation into the gas phase ever observed?

The question must be answered in the affirmative. The Haber-Just effect,[418] the emission of free electrons as a result of the action of phosgene on metallic sodium, represents one such process. Later, Polanyi and Bogdandy [419] bombarded solid sulphuric acid with atomic sodium and found that the hydrogen atoms resulting from the reaction were not catalytically recombined, but left the surface as accelerated atoms. The atoms, therefore, actually take up the reaction energy, in part as kinetic and in part as chemical energy, and can give up this energy later, in the gas phase; for example, by their recombination, they can excite sodium vapor to luminescence. Frommer and Polanyi [420] found exactly analogous processes in the action of chlorine simultaneously on aluminum and copper. There results, in a primary process from aluminum and chlorine, a volatile

[418] F. Haber and G. Just, *Z. Elektrochem.*, **20**, 483 (1914); *Ann. Physik.*, **36**, 308 (1911); *Physik. Z.*, **12**, 1035 (1911).

[419] M. Polanyi and St. v. Bogdandy, *Naturwiss.*, **14**, 1205 (1926).

[420] L. Frommer and M. Polanyi, *Z. physik. Chem.*, B **6**, 471 (1929).

unstable intermediate product which again carries its chemical energy away from the surface and gives it up again in further transformations in the gas phase, by exciting the simultaneously produced CuCl to luminescence. The two metals when treated with a stream of chlorine under suitable conditions of temperature and pressure are surrounded by a luminescent halo having the characteristic spectrum of CuCl. Frankenburger and Zimmermann [421] observed analogous luminescent effects from the simultaneous action of oxygen and nitrogen on lithium metal.

The condition that the chain initiator shall detach itself from the surface and pass into the gas phase is, therefore, fulfilled. One case is also quite certainly established in which a catalysis results in this manner. It is the phenomenon discovered by Haber and Alyea [422] of the more ready explosion of electrolytic gas when walls are present. We saw on page 52 that, in the free gas, electrolytic hydrogen and oxygen can only be exploded, at a given pressure, above a certain limiting temperature, because, at lower temperatures than this limit, fewer chains are started in unit time than are broken. It was shown that this limiting temperature was much higher, often as much as 100°, in a pure homogeneous reaction (with crossed gas streams) than when in contact with a wall (a quartz rod at the point of crossing of the streams) even though the temperature of the wall did not exceed that of the gas. Since the radicals H and OH are the chain carriers (page 42) it is pertinent to suggest that the primary reaction

$$H_2 + O_2 = 2OH$$

can be catalytically influenced. The wall would then be a source of OH molecules which react further in the gas phase to yield chains. According to investigations of Thompson, [423] mixtures of oxygen and carbon disulphide behave similarly.

In a recent paper[423a] Taylor has discussed a number of alternative mechanisms whereby such chain makers may be released into the gas phase. Actually the one above cited does not appear to be exothermic enough to result in the release of the radicals into the gas phase. Reactions between adsorbed oxygen or hydroxyls and impinging hydrogen molecules

$$S(O) + H_2 = S(OH) + H \uparrow$$

and

$$S(OH) + H_2 = S(OH_2) + H \uparrow$$

[421] W. Frankenburger and W. Zimmermann, *Z. physik. Chem.*, B **10**, 238 (1930).

[422] F. Haber and H. N. Alyea, *Naturwiss.*, **18**, 441 (1930); *Z. physik. Chem.*, B **10**, 193 (1930).

[423] H. W. Thompson, *Z. physik. Chem.*, B **10**, 273 (1930).

[423a] H. S. Taylor, *Chem. Rev.*, **9**, 1 (1931).

are suggested as mechanisms for the release of atomic hydrogen into the gas stream. Such proposals are regarded by Taylor as the mechanism where " active " hydrogen is produced by passage of the molecular gas over suitable surfaces. One research of this type in particular, that of Mitchell and Marshall [423b] demonstrated conclusively that production of " active " hydrogen did not occur on platinized asbestos when pure hydrogen was used. Small concentrations of oxygen down to 0.02 per cent were shown to produce the activation, combustion of hydrogen occurring during the process. The active hydrogen produced was unstable but persisted for a distance of 5 cm. from the activating surface under the experimental conditions. Taylor regards this as proof of the existence of atomic hydrogen in the exit gas stream in such experiments, and of one mechanism for the initiation of reaction chains.[423c]

This interesting subject has led, nevertheless, to erroneous observations and calculations. Kobosew and Anochin [423d] thought that they could show the free hydrogen atoms produced in the heterogeneous reaction of hydrogen and oxygen by its reducing action on WO_3 and the development of a blue color. Roginsky and Zeldowitsch [423e] were able to show, however, that this effect occurs, if at all, by reason of overheating, localized at the reduction areas.

Bennewitz and Neumann [424] have attempted, with a striking experimental arrangement, to demonstrate a chain initiation in heterogeneous catalysis which had formerly been thought to occur exclusively in the surface. They chose the hydrogenation of ethylene on platinum as the example to be studied. They first showed theoretically, by calculating the impulse effects to be anticipated, that, in the stationary state and with adsorption equilibrium, for every ethane molecule leaving the surface, and a hydrogen and ethylene molecule reaching the surface inclastically, the catalyst must suffer a mechanical impulse. In this special case calculation shows a suction into the gas, the magnitude of which must be calculable from the amount of reaction. If the catalyst was arranged as a torsion balance or radiometer vane it must experience a turning motion. Older researches of other investigators on other non-catalytic reactions confirmed the correctness of this conclusion.

The experiments showed, however, that the anticipated torsion of the platinum vane was entirely absent, but a small pressure effect occurred

[423b] A. E. Mitchell and A. L. Marshall, *J. Chem. Soc.*, **123**, 2448 (1923).
[423c] See also H. N. Alyea, *J. Am. Chem. Soc.*, **53**, 1324 (1931).
[423d] Kobosew and Anochin, *Z. physik. Chem.*, B **13**, 63 (1931).
[423e] S. Roginsky and Zeldowitsch, *Z. physik. Chem.*, B **18**, 361 (1932).
[424] K. Bennewitz and W. Neumann, *Z. physik. Chem.*, B **7**, 247 (1930).

which was attributed to a heat effect of the reaction not previously taken into account. From the absence of the torsion effect the authors concluded that, at the most, one thousandth part of the total reaction actually occurred at the surface of the contact mass, while the major portion of the conversion occurred as a chain reaction, homogeneously, presumably with hydrogen atoms and free ethyls as intermediate stages.

It does not seem that this assumption can be considered as entirely established, since still other possibilities of interpretation exist at least in principle, and a chain mechanism can fundamentally only be regarded as demonstrated if it is also supported by reaction kinetic measurements. Attempts by H. S. Taylor and D. J. Salley [424a] to produce such a chain reaction by means of atomic hydrogen in hydrogen-ethylene mixtures at high temperatures were unsuccessful. Also Schuster [424b] came to the conclusion that the reaction occurred exclusively on the catalytic surface. Foresti [424c] has recently applied a micro-calorimetric method to the same problem and also concludes that the reaction occurs exclusively on the surface. He states that a private communication from Bennewitz reveals that the latter has been unable to confirm the earlier results of Cantor [424d] with non-catalytic reactions and could not obtain a rotation of the experimental vane. The earlier result of Bennewitz and Neumann must, therefore, be ascribed to the experimental conditions, as they have themselves, more recently, stated.[424e]

Christiansen [425] has undertaken the problem of studying a possible chain reaction from the standpoint of kinetics. He had found that the reaction

$$CH_3OH + H_2O = CO_2 + 3H_2$$

at magnesia surfaces occurs according to a reaction equation in which the product of the concentrations appears in the denominator. We have already seen (page 222 et seq.) that the application of the Langmuir isotherm to kinetics, results in summations of terms with bp, but never the product of such, in the denominator of the velocity expression. On the other hand, such terms in the denominator of the velocity equation for chain reactions (page 51) are to be expected:

$$\phi = \phi_1 \frac{w}{1 - pw}$$

[424a] H. S. Taylor and D. J. Salley, unpublished experiments in Princeton, 1931.
[424b] C. Schuster, *Z. physik. Chem.*, B **14**, 249 (1931).
[424c] B. Foresti, Ateneo Parmense, IV, 401 (1932).
[424d] M. Cantor, *Ann. Physik.*, **62**, 482 (1897).
[424e] Bennewitz and Neumann, *Z. physik. Chem.*, B **17**, 457 (1932).
[425] J. Christiansen and J. R. Huffman, *Z. physik. Chem.*, A **151**, 269 (1930); *Phys. Chem. Konf.*, Leningrad, 1930; *Z. physik. Chem.*, Bodenstein Festband, 69 (1931).

since the probabilities w are generally products of the individual probabilities of the successive reactions. Hence, Christiansen concludes that his reaction is a chain reaction and that this possibility has general significance.

Even this argument is not final for, with the possibility of adsorptions in different areas without displacement (page 230), heterogeneous mechanisms also yield products of the concentrations and, precisely with the mixed catalyst employed, Cu—MgO, such a possibility cannot be excluded.

In any case, heterogeneous chain catalysis would be well to keep in mind. Christiansen leaves open the question whether the chains occur in the gas phase or on the surface. The latter is suggested for two reasons: in the first place, we now know that a two-dimensional motion of the adsorbate can occur under certain conditions and secondly, we have already seen the possibility of the preferential existence of active products in the surface by reason of their free valences and consequent high heats of adsorption.

Two examples may be cited in which such a representation can possibly be brought forward. We recall that ammonia decomposes on platinum according to a velocity equation

$$\frac{dx}{dt} = k \frac{[NH_3]}{[H_2]}$$

and with an apparent activation energy of 44 kilocals. On other metals, the mechanism is the same, with a possible variation in the degree of retardation, and with an activation energy which differs but little. At pressures, however, greater than about 10 mm., the mechanism on platinum is quite different; the equation now has the form:

$$\frac{dx}{dt} = k \frac{[NH_3]}{[H_2]} \cdot \frac{[NH_3]}{[H_2] \cdot ([H_2] + b\,[NH_3])}$$

and the apparent activation energy is around 140 kilocals.[294] The increase in the activation energy of approximately 100 kilocals. is so considerable that heats of desorption of the reaction products (see page 238) can surely not be the cause. Also the velocity equation is only with difficulty interpretable on the basis of a Langmuir isotherm. If, on the other hand, there is a chain reaction, the high temperature coefficient can quite simply arise, according to a private communication of Dohse and Dunkel, from an increase in chain length with increase of temperature, a rise which overwhelms the normal increase of the primary process. This is rendered more probable also by the occurrence of the products of the concentrations in the denominator. At lower pressures such a chain would not occur. Nor is there a chain in

streaming gases at a platinum gauze, where Dixon [425a] finds an activation energy of 40 kilocals.

As the second example, mention may be made of the decomposition of nitrous oxide on platinum which van Praagh and Topley,[291c] owing to the poor reproducibility of their measurements and those of Schwab and Eberle,[291a] are inclined to regard as a surface chain with critical inflammation limits.

The one case in which one may, with great certainty, expect a homogeneous chain following a surface initiation is, according to Roginsky and Zeldowitsch,[423e] the catalytic ammonia oxidation reaction, of which Bodenstein [425b] has recently treated the problem of mechanism.

Negative Heterogeneous Catalysis

Under this heading is to be understood the phenomenon of a diminution in reaction velocity due to a substance present in a separate phase. At first glance, what has already been said concerning homogeneous negative catalysis applies *a fortiori* to such cases; it cannot easily be seen how the velocity of a homogeneous gas reaction somewhere in space can be diminished by the presence somewhere else of a wall with certain properties. On the contrary, inhibition is obviously understandable when the reaction is a chain reaction which is broken at the wall.

We have already recognized a number of these retardations at an earlier stage when we discussed, for example, as homogeneous catalysis, the influence of gaseous additions on chain breaking at the wall (page 54). We wish to mention this once more here and somewhat amplify it.

Hinshelwood and Thompson [73] and also Gibson and Hinshelwood [74] found that the slow combustion of hydrogen-oxygen electrolytic gas between 550° and 570° C. was not accelerated by increase of wall surface, as it was at lower temperatures, but was retarded; that, therefore, in this region, the reaction is homogeneous, the chains breaking at the walls.

The catalytic ignition of hydrogen-oxygen mixtures by nitrogen dioxide is raised to higher temperatures by increase of the surface area of the reaction vessel because, according to Norrish and Griffiths,[54a] the chains are broken not only by nitrogen dioxide in the gas phase but also heterogeneously at the walls.

In other cases it can explicitly be stated which intermediate products are removed by the wall. Thus, Jost and Jung [72] showed that the combination

[425a] J. K. Dixon, *J. Am. Chem. Soc.*, **53**, 2071 (1931).

[425b] M. Bodenstein and G. Büttner, Trab. del IX Congr. Intern. de Quimica, II (1933); see also M. Bodenstein, *Helv. Chim. Acta* **18**, 743 (1935).

of bromine and hydrogen in light at low pressures is retarded by the wall in that the recombination of bromine atoms which propagate the chain does not occur, as at higher pressures, by three-body collisions in the gas phase, but by such collisions with the wall as third body. We have seen already that the prevention of diffusion due to foreign gases retards such wall recombination. In a quite analogous manner the chlorine atoms in the photochemical formation of phosgene are the atoms which disappear at the wall.[48] Since this disappearance occurs as a first order reaction, our derivation of the $\sqrt{Cl_2}$ law on page 48 is not strictly applicable to the light reaction; in principle, however, it stands, because another intermediate, ClO, recombines homogeneously according to the second order relation.

Polanyi, Bogdandy and Hartel [87, 88] show that the chains of the sodium-induced hydrogen-chlorine and methane-chlorine reactions are broken at the walls of the vessel due to the disappearance of the intermediary substances H, CH_3 and Cl.

For the photochemical hydrogen-chlorine reaction such a termination of chains at the walls was formulated by Cremer [67] and rendered plausible by the observation that the form and magnitude of the velocity varies with the nature of the material and cleanliness of the wall surface. This assumption was then directly confirmed by Trifonoff.[140] With decreased pressure, the probability that the chains are broken by oxygen in the gas phase must progressively decrease in favor of chain-breaking at the wall. Trifonoff found that the increase of hydrogen chloride concentration at high pressures is independent of the size of the vessel, because, in such case, it was a question of a pure volume effect, that is to say, the chains were broken homogeneously. Below 30 mm. pressure, however, the velocity of diffusion has become so large that now the velocity of reaction is proportional to the square of the diameter of the vessel; this is to be expected, however, if the diffusion to the walls causes the chains to be broken. At still smaller pressures (below 0.21 mm.) the reaction stops completely because all the chains are broken before they get really under way. According to newer observations of Bodenstein and Unger,[426] in this example, only the first stage of the chain-breaking is a wall reaction, resulting in a gaseous compound with the wall material, presumably SiCl. The second process is then a homogeneous combination of chlorine atoms with this intermediate. Similar results to those in the hydrogen-chlorine chain have also been found by Sprenger [427] in the decomposition of nitrogen pentoxide at low pressures. His observations on the incompleteness of the decomposition in the pres-

[426] M. Bodenstein and W. Unger, *Z. physik. Chem.*, B 11, 253 (1931).
[427] G. Sprenger, *Z. physik. Chem.*, 136, 49 (1928).

sure region 0.01 to 0.05 mm. have not been substantiated in their extreme form by later more accurate work,[427a, b] though qualitative indications are present to a minor degree in the work of Ramsperger and Tolman. The modern theory of unimolecular reactions accounts fairly well for the data in this reaction down to pressures of 0.005 mm.

Of other examples of this type there may be mentioned the action of anti-knock agents (page 62 et seq.) which, according to Bodenstein,[93, 230] can also be explained by a breaking of explosion chains at the solid surface of the metal particles. Also, the suppression of flame at the mouths of cannon after firing, by the addition of potassium chloride to the powder, must be dependent on a breaking of reaction chains occurring in the flames, at the surface of the salt crystals. Taylor and Lavin,[427c] in a research on this subject, indicated the efficiency of potassium chloride surfaces in the recombination of the fragments of the water molecule produced in a high tension water discharge tube.

We, therefore, see that we have to do with a very general principle. And there is also a very general explanation for this action of the walls. It is the three-body hypothesis of Born and Franck [79] which we have already made use of in the breaking of chains homogeneously, that is, the assumption or even the fact that addition reactions of the simpler reaction systems occur more frequently or even only when a third partner in the collision, for example, a solid wall, is present, which can conduct away the resultant heat of reaction. We can, therefore, understand why retardation by walls is so general a phenomenon.

These recombination reactions at the walls, deduced indirectly from chain reactions have also been observed directly. The influence of the containing walls on hydrogen atom recombination will be discussed shortly. The recombination of chlorine atoms produced by electric discharge has been studied by Schwab and Friess,[427d] that of bromine atoms by Schwab.[427e]

For free methyl and ethyl radicals, resulting from the decomposition of metal alkyls, there is the work of Paneth and his collaborators.[427f] In all these cases, it has been shown that they do not recombine in the gas phase according to a second order reaction but only on the vessel walls as a first order process. They recombine at rates determined by their rate of con-

[427a] H. C. Ramsperger and R. C. Tolman, *Proc. Nat. Acad. Sci.*, **16**, 6 (1930).
[427b] H. J. Schumacher and G. Sprenger, *ibid.*, **16**, 129 (1930).
[427c] H. S. Taylor and G. I. Lavin, *J. Am. Chem. Soc.*, **52**, 1910 (1930).
[427d] Schwab and Friess, *Z. Elektrochem.*, **39**, 586 (1933).
[427e] Schwab, *Z. physik. Chem.*, B **27**, 452 (1934).
[427f] Paneth and Herzfeld, *Z. Elektrochem.*, **37**, 577 (1931); Paneth and Lautsch, *Ber.*, **64**, 2708 (1931).

tact with the walls. The extinction of the glow of active nitrogen on walls which have not been poisoned is similarly explained.[427g]

On the other hand, there is, however, an undoubted specificity of wall surface. According to Cremer, moist glass walls have a capacity to assist the recombination of chlorine atoms which dry quartz surfaces do not possess.

Direct observations [427d] show that at metal surfaces every colliding atom disappears. At glass and quartz, according to conditions, every 10th to 70th atom disappears. Paneth [427f] has shown that, in the case of his free radicals, the collision efficiency for recombination lies between one and one-thousandth. Also, the recombination of hydrogen atoms on metals and the like, studied by Bonhoeffer,[76] does not occur if the wall is covered with a layer of water vapor, as is confirmed by the work of Senftleben and Riechemeyer [83] or that of von Wartenburg and Schultze.[428] Polanyi finds [87, 88] that the breaking of his induced chains is thirty times slower with the surfaces of sodium chloride produced in the reaction than with the original glass surface. As we have already seen (page 64) the anti-knock effect cannot be produced by every species of solid body but that metals are especially suitable and we have already noted the chemical conclusions to which this observation leads.

Here also, the cause of the selectivity must be associated with a selective chemical affinity, that is to say, in heterogeneous processes, a selective adsorption. Since all the processes which produce breaking of chains are, reaction-kinetically, processes of the first, and not second, order, an adsorption of one of the two partners must have preceded the actual three-body collision, so that the second partner at, or after, its arrival at the wall must certainly collide with the one already present. It is also to be pointed out that the ready adsorbability of active atoms or radicals follows directly from our observations on adsorption. Since this adsorption is governed by specific valence forces it is understandable that its activity can also be specific. With bromine atoms, the adsorption is so strong [427e] that, even on glass, every colliding atom meets a partner, a result which is in agreement with the photochemical results (see later).

So soon, however, as the activity of the collisions at the wall exceeds a certain degree, the reaction itself will no longer determine the velocity, in agreement with the introductory observations on page 221; on the contrary, the slower diffusion to the wall will be the determining factor. Especially in the case of recombination of atoms, in which, indeed, the presence of the wall is oftentimes a sufficient condition for a reaction without

[427g] E. J. B. Willey, *J. Chem. Soc.*, 1146 (1930).

[428] H. von Wartenburg and G. Schultze, *Z. physik. Chem.*, B 6, 261 (1929).

activation energy, this condition can often hold, and obedience to the laws of diffusion then supplies the best proof for the theory of retardation by the walls, and in many cases, in fact, the point of departure for its quantitative development.

According to a gas-kinetic formula of Smoluchowsky the time t, which a particle requires to traverse a distance x^* by diffusion, is given by the expression

$$t = \frac{3\pi x^2}{4Lc}$$

where L is the mean free path, c the mean molecular velocity. With active particles in diffusion, x is obviously the average path which the chains travel in the free gas before they are broken at the wall, and, therefore, equal approximately to the radius of the vessel; the time t which the diffusion requires is a measure of the chain length. This is, however, precisely the result obtained by Trifonoff (page 318) in which, at low pressures, the chain length is proportional to the square of the diameter of the vessel; herein, therefore, is the best evidence of chain-breaking at the walls. On the other hand, with this formula, the frequency of chain-breaking, that is to say the constant k of the chain-breaking partial reaction, can be calculated from the dimensions of the vessel and the magnitudes L and c at the given concentrations and temperature. Such calculations are also in agreement with experiment. It is, therefore, understandable why the breaking of chains is first noticed at low pressures, that is with large values of L, as was found in the case of bromine by Jost and Jung, and as Bodenstein, Lenher and Wagner found quantitatively with chlorine atoms in the phosgene reaction. Indeed, it is often possible, from the value of the constant for the chain-breaking reaction, to calculate the other reaction constants in the velocity equations for the chain, and thus arrive at values which, especially in the last mentioned example, show the right relation of absolute values and temperature coefficients of bimolecular reactions

$$k = Z\, e^{-E/RT}$$

In this manner, the termination of chains at wall surfaces offers the possibility of separating the chain reactions themselves not only formally, but even quantitatively, into their separate stages.

* x is strictly not the mean displacement but the square root of the mean square displacement, x^2.

CHAPTER XVIII

CATALYSIS IN SOLID SYSTEMS

We turn now to a discussion of cases, which, at the outset, were set on one side, in which the substrate rather than the catalyst is the denser aggregate, more especially Cases VI, VII and VIII mentioned on page 179 with gaseous, liquid and solid catalysts, respectively. In such cases, on account of the different mobilities of the materials in question, the kinetics are completely changed and, on account of the changed cohesions of the materials, the energetics and also the adsorption phenomena are completely different. Besides catalysis which depends upon the principle of deformation due to the effects of valence, we also deal here with quite new types of reaction acceleration.

Gaseous Catalysts

The reactions of solid phases accelerated by gases are obviously rare, since, as we have seen, the influence of these on solid substrates is not very pronounced. Cases which have been observed appear, therefore, to be attributable to other factors. W. Jander and W. Stamm [429] find that certain reactions in the solid state are markedly accelerated by the presence of water vapor. The systems in question are

$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$La_2O_3 + 3SiO_2 \rightarrow La_2Si_3O_9$$
$$BaCO_3 + SiO_2 \rightarrow BaSiO_3 + CO_2$$
$$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2$$
$$BaCO_3 + WO_3 \rightarrow BaWO_4 + CO_2$$

For the final example cited, it is seen in Fig. 39, that the velocity is increased without any marked change in the activation energy, given by the slope of the logarithmic plot.

To obtain an interpretation of catalysis by water vapor in such processes it is first necessary to form a picture of such reactions between two

[429] W. Jander and W. Stamm, *Z. anorg. allg. Chem.*, **190**, 65 (1930).

solid phases, such as is given in the researches of Tammann cited by Jander and Stamm. According to this picture, there results at the point of contact of two reacting particles a layer of reaction product, and the diffusion of one or both reactants through this layer by exchange of positions of adjacent units is the rate-determining process that is measured. The " activation energy " is therefore in these cases the critical vibrational energy or " heat of disruption " which permits a component to exchange its position in the lattice of the reaction product. This magnitude will not be reduced by water vapor in the manner familiar in adsorption catalysis. The fact, however, that the diffusion, or the number of particles with the necessary mobility, is increased is to be explained, according to Jander, in two ways: water can dissolve in the lattice thus expanding it and so increasing the velocity of motion of the particles; or it may give rise to more finely divided particles of product with more Smekal cracks [392] or more possibilities of edge diffusion as discussed by Schwab and Pietsch.[252]

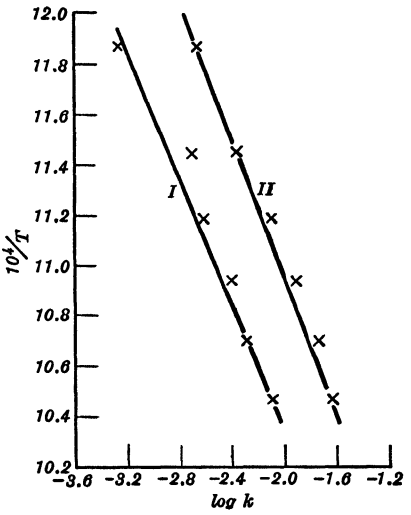


FIG. 39. Catalysis by Water Vapor of the Reaction between Barium Carbonate and Tungstic Oxide (Jander). I Spontaneous. II Catalyzed.

Spencer and Topley [430] decide in favor of this latter possibility. They find an acceleration of the reversible reaction,

$$Ag_2CO_3 = Ag_2O + CO_2,$$

by water vapor. They consider the best explanation to be that the adsorption of water vapor, that is to say, possibly, the formation of a silver hydroxide, facilitates the diffusion of carbon dioxide to and from the material over the surface and interfaces.

In another case, the decomposition reaction,

$$MnC_2O_4 \cdot 2H_2O \rightarrow MnC_2O_4 + 2H_2O,$$

Topley and Smith [430a] believe that they must assume a real deformation-

[430] W. D. Spencer and B. Topley, *J. Chem. Soc.*, 2633 (1929); *Trans. Faraday Soc.*, **27**, 94 (1931).

[430a] B. Topley and J. W. Smith, *Nature*, August 22 (1931).

catalysis as a result of polarization at the interface hydrate-anhydride. The definitely observed catalysis of the reaction sulphur-silver by means of water vapor, discovered by Smith [430b] remains as yet unexplained.

Liquid Catalysts

In the daily experience of chemists there are so many examples of this type of catalysis known, that it is perhaps superfluous to cite special illustrations. It is a generally well known fact that reactions between solid substances, for example, the transitions from one form of solid sulphur or phosphorus to another, are greatly accelerated if solvent or, better, saturated solution is in contact with both phases. The reasons for such accelerations can be of the most varied character. In one case the solution itself can actually operate as the medium of increased reaction velocity, in the sense, therefore, of a deformation-catalysis (page 179). On the other hand, we have already seen, and will also learn from subsequent sections, that reactions in the solid state are subject not only to quite characteristic retardation due to slow diffusion but also to a topochemical limitation to interfaces. Both these difficulties are excluded if the process occurs via the path, solution, homogeneous reaction, precipitation.[430c]

In addition, the action of a liquid may consist in the displacement of a retarding surface layer, such as an oxide surface, thereby facilitating the contact of the reacting components. This is the function, for example, of fluxes such as zinc chloride, colophony, ammonium chloride or borax used in soldering.

Solid Catalysts

We come next to the most important and interesting of the three cases in which one solid accelerates the reaction of another. In the sense that the reaction product itself exerts this accelerating effect, practically all reactions in the solid state are catalytic. We shall cite only a few of these cases which have been studied in more detail. We follow in this respect the treatment of Volmer [431] and of Schwab and Pietsch.[252] Langmuir [431a] was the first to call attention to the quite general significance of reactions at the boundary of phases in the kinetic mechanism of heterogeneous

[430b] J. W. Smith, *J. Chem. Soc.*, 860 (1931).

[430c] For literature on processes of this kind see W. Feitknecht, *Fortschr. Chem., Physik., u. physik. Chem.*, **21**, Heft 2 (1930); Topochemical Reactions of Solid Substances in Liquids.

[431] M. Volmer, *Z. Elektrochem.*, **35**, 555 (1929).

[431a] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2263 (1916).

equilibria involving solid substances. The applicability of the concept of Langmuir to the problem of catalysis by solid substances and to the phenomenon of promoter action was emphasized by Taylor in a discussion [431b] covering most of the following examples and others:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$
$$2Ag_2O = 2Ag + O_2$$
$$AgMnO_4 = AgMnO_3 + \tfrac{1}{2}O_2$$
$$S_{(monocl.)} = S_{(rhomb.)}$$
$$CuO + H_2 = Cu + H_2O$$
$$NiO + H_2 = Ni + H_2O$$
$$CuSO_4 \cdot 5H_2O = CuSO_4 \cdot 3H_2O + 2H_2O$$
$$BaCl_2 \cdot 2H_2O = BaCl_2 + 2H_2O$$
$$Ag_2C_2O_4 = 2Ag + 2CO_2$$
$$6Li + N_2 = 2Li_3N$$
$$3Ca + N_2 = Ca_3N_2$$
$$Hg + I_2 = HgI_2$$
$$2KMnO_4 = K_2O + 2MnO_2 + 1\tfrac{1}{2}O_2$$

It is the solid reaction product which, in each case, acts as catalyst. In the final example, the manganese dioxide is the catalyst. The reactions are all characterized by the fact that the new phase itself acts as the catalyst. The reactions, therefore, occur solely where the substrate is in contact with the product. As a consequence, the process consists in an increase of the reaction product at the cost of the reactant in a progressive displacement of the phase boundary between them. In many cases, as, for example, in the efflorescence of salt-hydrates, the sulphur transition, nitride formation, the reduction of copper oxide, and the formation of mercuric iodide, this growth of reaction product can be observed visually.

In other cases, this behavior is deducible with certainty from the reaction kinetics. The characteristics of this, as of all autocatalytic reactions, is that the reaction velocity initially rises, in these cases because the size of the interfaces increases, then reaches a maximum and finally falls, because the interfaces again become smaller by reason of the consumption of the reactant phase. This kinetic procedure was first observed by Lewis [432] in the decomposition of silver oxide.

We wish to consider the kinetics of such a case more closely, the decompo-

[431b] H. S. Taylor, *J. Franklin Inst.*, **197**, 1 (1922); Treatise of Physical Chemistry, Chap. XV, page 981, D. Van Nostrand Co., New York, 1st edition 1924; Third Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, **28**, 933 (1924).

[432] G. N. Lewis, *Z. physik. Chem.*, **52**, 310 (1905).

sition of potassium permanganate, with reference to the data of Roginsky and Schultz.[331] In the first place, there must be present centers from which the reaction can start, the so-called reaction-nuclei. We can think of these also as active centers present on the surface at corners and edges or arising from a heating of the material. If the velocity of formation of the nuclei is rate-determining for the whole process, that is to say, if the nuclei, once formed, grow so rapidly that they immediately "eat up" the whole granule, the reaction will be one of first order, without autocatalysis.[433] If, on the other hand, there are initially so many nuclei present that they cover the whole surface, there will spread out from the surface into the interior a spherical area of reaction product with decreasing surface content, that is to say, there will again be no autocatalysis. Spencer and Topley [430] observed this case in the dissociation of silver carbonate. In the case of potassium permanganate, also, the period of auto-acceleration is markedly shortened by finely powdering the material, a procedure which increases the number of nuclei at the surface.

On the contrary, a more characteristic case is that in which the nuclei are so far distant one from another that they do not grow with one common interfacial area, but yet are numerous enough that their growth and not their rate of formation determines the reaction velocity. In such case each nucleus grows to a sphere with increasing surface and, only when these spheres come into contact one with another and grow together, does the interfacial area and so the velocity decrease.

Let the content of such a zone or sphere be x, and its surface, S. Then it follows that

$$\frac{dx}{dt} = S \cdot const.$$

or, since,

$$S \propto x^{2/3},$$

$$\frac{dx}{dt} = k \cdot x^{2/3}.$$

Let there be N nuclei present. The total reaction in time t amounts therefore to

$$X = Nx,$$

and the velocity to

$$\frac{dX}{dt} = \frac{kX^{2/3}}{N^{2/3}}.$$

The velocity therefore first rises proportionally to the two-thirds power of the material already converted. With potassium permanganate which was

[433] B. Topley and J. Hume, *Proc. Roy. Soc.*, A 120, 211 (1928).

not too coarse, Roginsky and Schultz confirmed such a rise. Topley and Hume [433] find the same result, or at least a closely related formula, for the initial stages in the dehydration of $CaCO_3 \cdot 6H_2O$.

Towards the close of the reaction there remains only a wedge of reactant between the coalescing spheres of reaction product. These decrease again proportionally to their surface; hence,

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k'(a-x)^{\frac{2}{3}}$$

and

$$\frac{dX}{dt} = \frac{k'}{N^{\frac{2}{3}}}(A-X)^{\frac{2}{3}}.$$

In both cases cited, the velocity approaches zero towards the end of the reaction at rates which agree with this formula. The following reactions also obey these velocity equations, the reduction of copper oxide [309] and nickel oxide [434] by means of hydrogen or carbon monoxide,[435] the conversion of one form of sulphur into another [436] and all the reactions set forth above.

The question at once arises why this autocatalysis is apparently so general a law in reactions of the solid → solid type. There is a very general thermodynamic basis for this [252, 431] which was first clearly pointed out by Ostwald in the case of gypsum. " That such forms result at all, can only be understood if one assumes that the efflorescence can only occur at those places where hydrate and anhydrite touch each other, since the condition for a definite dissociation pressure, the coexistence of both phases, holds only at such positions. The homogeneous part of the crystal has as little influence on the value of the dissociation pressure as the completely dehydrated material."

This point of view, first applied to the dehydration of gypsum, can obviously be generalized. Langmuir [437] expressed it in another form, that of an indirect proof: Let us assume that gypsum could be formed from anhydrite and water vapor over the whole surface of anhydrite and also that anhydrite could be formed by evaporation of water from any area in the surface of gypsum; then, by making the same assumptions for the forward and backward reactions, as in the derivation of the Langmuir absorption isotherm, it follows that the velocity of formation of gypsum is

$$k_1 \cdot p \cdot \text{Anhydrite surface},$$

[434] A. F. Benton and P. H. Emmett, *J. Am. Chem. Soc.*, **48**, 632 (1926).
[435] W. G. Palmer, *Trans. Am. Electrochem. Soc.*, **57**, 445 (1927).
[436] W. Fränkel and W. Gotz, *Z. anorg. allgem. Chem.*, **144**, 45 (1925).
[437] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2263 (1916).

while its velocity of decomposition is

$$k_2 \cdot \text{Gypsum surface.}$$

For the equilibrium pressure of the water we thus obtain:

$$p = \frac{k_2}{k_1} \times \frac{\text{Gypsum surface}}{\text{Anhydrite surface}}.$$

Since, however, the phase rule (three phases, two components and, hence, only one degree of freedom, the temperature) demands a definite dissociation pressure, this dependence of pressure on the extent of phase surface is false and a change can, therefore, only occur in both directions at the same surface. Such a surface, which permits both changes to occur is, however, only the boundary of the two phases. The change is localized at this position. In the case of mixed crystals this naturally does not hold, but even in these systems the reactions occur usually more rapidly than the equalization of concentration in the mixture by diffusion.

This thermodynamic treatment does not include, however, any interpretation of the catalytic mechanism which brings about the localization of the reaction at the phase boundaries. In particular, it applies only to the equilibrium condition and, like all thermodynamic derivations, determines nothing as to the velocity under circumstances far removed from the equilibrium state. And the phenomenon is considered, in the main, with processes in which the back reaction is far outside the region of experimental measurement.

The question, therefore, to be answered is what molecular mechanism is responsible for the reaction proceeding so very much faster at the phase boundaries than that occurring with negligible velocity in the interior of a phase. There are two possibilities that we have already touched upon. We may choose as an example, with Volmer, the reaction

$$2Ag_2O = 4Ag + O_2$$

which was studied by Lewis. We can separate it into two stages, firstly, a purely chemical decomposition of the oxide into silver atoms and oxygen molecules,

$$(1)\ 2Ag_2O = 4Ag_{(gas)} + O_2,$$

and, secondly, the deposition of the silver on the nuclei of crystalline silver already present,

$$(2)\ 4Ag_{(gas)} = Ag_{4(solid)}$$

If now reaction (1) is the rate-determining process the catalysis involves a

purely chemical process, hence a diminution of the activation energy by adsorption and deformation at the active boundary lines.[262]

This is the case in a series of dissociations of carbonates, in which no activation energy other than the thermochemical heat of reaction is necessary.[437a] In such cases, where the opening up of the initial lattice is velocity determining, one can understand why Jander and Hoffman [437b] find that foreign substances do not materially lower the dissociation energy expended, but only increase the number of nuclei. If, however, the second reaction determines the rate, that is to say, if the reaction finally ceases until the silver vapor formed, finding no nuclei of crystallization present, builds up to the equilibrium concentration of reaction (1), then solid silver present operates simply as a nucleus, preventing supersaturation of silver vapor with respect to solid silver; it induces an ordered separation of silver by reason of an orienting action on adsorbed silver atoms.

This second action is only possible if the equilibrium in (1) lies at such silver pressures that a spontaneous formation of nuclei is not possible. For spontaneous formation of nuclei, a definite degree of supersaturation obtains which limits the " metastable region " and which can be estimated from the surface tension of the substance being formed (Volmer [431]).

In the preceding example of silver, the establishment of equilibrium in reaction (1) leads to a supersaturation of silver vapor of about 10^4 fold, and the estimate of the metastable limits indicates that a supersaturated vapor of such a kind is not certainly able to produce spontaneous crystallization. There is, therefore, the possibility that, in this case, only reaction (2) is accelerated due to orientation.

For the reaction studied by Pease and Taylor,[438]

$$CuO + H_2 = Cu + H_2O,$$

and the reverse reaction with oxygen, both of which are autocatalytic (see page 232), Okayama [341] has applied the same considerations and has reached the opposite conclusion. The oxidation is catalyzed by copper oxide even with 10^{18} to 10^{30} fold supersaturation and the reduction process is catalyzed by copper even with a 10^{15} fold supersaturation. These are values at which one might definitely expect spontaneous crystallization. In this case, therefore, we have to assume a real catalysis of reaction (1) involving the activation energy of the process. It is, however, difficult to set a limit

[437a] K. Fischbeck and Schnaidt, *Z. Elektrochem.*, **38**, 199 (1932).

[437b] Jander and Hoffman, *Z. anorg. Chem.*, **202**, 135 (1931).

[438] R. N. Pease and H. S. Taylor, *J. Am. Chem. Soc.*, **43**, 2179 (1921); **44**, 1635 (1922).

since Estermann,[439] for example, did not observe the action of solid cadmium as nuclei in a vapor of cadmium 10^{10} fold supersaturated.

It is, nevertheless, generally very probable that, besides the catalysis due to operation as nuclei, true catalysis by reduction of the activation energy is also involved. The boundaries of the granules at which the reactions occur are the lines of especially unsaturated character at which synergetic effects are to be expected. That this is so is directly supported by other observations: the reaction product can often be replaced by other substances.

The accelerated decomposition of silver oxide in contact with platinum is still not proof that this is not due to nuclei formation since it has frequently been observed that a foreign substance which is crystallographically similar can so act. Examples of such behavior are cited by Schwab and Pietsch.[252] But manganese also accelerates this reaction although it certainly cannot form nuclei for silver crystals. Taylor [431a] has cited the researches of Kendall and Fuchs [439a] on the accelerated decomposition of silver oxide, mercuric oxide and barium peroxide in presence of other oxides as examples of the replacement of the reaction product by other materials as catalysts in such interface decompositions. As also emphasized by Taylor,[431a] the case of mercuric oxide at 500° C. is especially interesting as, alone, mercuric oxide produces no interfaces owing to the volatility of the mercury. Hence, the equilibrium pressures are extremely slowly attained with pure materials, whereas they are established rapidly in presence of such added agents as iron oxide, manganese dioxide and platinum.[439b] The decomposition of silver permanganate studied by Sieverts and Theberath [440] is accelerated even by powdered pumice stone; the formation of calcium nitride is accelerated by sodium, probably in the form of nitride.[441] Roginsky, Sapogenikoff and Kutscherenko [442] find that the decomposition of mercuric oxide is very markedly accelerated by the oxides of nickel, iron, manganese, cobalt, copper, lead, zinc, chromium and cadmium, whilst the oxides of magnesium, titanium silicon, uranium and aluminum accelerate the decomposition five or six-fold. These results extend the observations of Hulett and G. B. Taylor [439b] cited above.

The decomposition of potassium permanganate studied by Roginsky

[439] J. Estermann, *Z. Elektrochem.*, **31**, 441 (1925).

[439a] J. Kendall and F. J. Fuchs, *J. Am. Chem. Soc.*, **43**, 2017 (1921).

[439b] G. A. Hulett and G. B. Taylor, *J. Phys. Chem.*, **17**, 567 (1913).

[440] A. Sieverts and H. Theberath, *Z. physik. Chem.*, **100**, 463 (1922).

[441] A. v. Antropoff and E. Germann, *Z. physik. Chem.*, A **137**, 209 (1928).

[442] S. Roginsky, L. Sapogenikoff and N. Kutscherenko, *Chem. Zentralbl.*, 1929 II, 2747, *Ukrain. Chem. J.*, **4**, 99 (1929).

and Schultz [331] is strongly accelerated by the oxides of Ni, Co, Mn^{IV}, Fe, Cu, less strongly by the oxides of Mn^{III}, Ag, Sn, Pb, Cr, Al, and not at all by the oxides of W^{IV}, Mg, Ca, Si. In this last case, especially, it is apparent that it cannot be any question of isomorphism; that, on the contrary, in general, those substances are good catalysts which are darkly colored, possess, therefore, strongly deformed and deformable electron structures in the sense discussed by Fajans, that they are frequently paramagnetic (unpaired electrons) and are often conductors of the first class. We have already recognized such materials as good deformation catalysts.

From such observations, it seems to follow that, in the case of autocatalysis and catalysis by added agents in reactions of solid substances, we are dealing with a process which is, in principle, similar to the diminution of activation energy by active centers in other heterogeneous catalysis.[442a] Therein lies not only an important conclusion in respect to these reactions, but this fact permits the reversed conclusion that the boundary lines which separate the chemically different areas of the surface are actually to be regarded as the regions of modified and enhanced activity, as the active centers of Taylor's theory. Hence, all the conclusions that we have already reached as to the activity of edges and especially of boundaries of granules and, above all, the important concept of synergy in mixed catalysts are thereby placed on a firmer basis.

The observations of Hedvall (page 294) are in close relation to this situation. He finds that chemical reactivity and, perhaps, also, catalytic activity of substances in the state of change are enhanced. In this state, as we have already set forth, many phase boundaries are formed within the material.

This does not, however, mean that the processes of reorganization in the production of a new phase should at once lead, in the immediate neighborhood of the reacting zone, to a completed lattice of the reaction product. Rather, with Hüttig, we envisage active intermediate states. If these intermediary phases do not attain molecular thicknesses,[442b] which is true according to Afanasiew and Roginsky,[442c] they are identical with the phase boundaries of our discussion. Otherwise, they make the picture somewhat more complex and are possibly responsible for many complications.[442d]

[442a] Indeed, it may be stated quite definitely that the recognition of the importance of these interface reactions was a major factor in the development of the concept of active centers. Tr.

[442b] C. Slonim, *Z. Elektrochem.*, **36**, 439 (1930).

[442c] P. Afanasiew and S. Roginsky, *Z. physik. Chem.*, B **18**, 360 (1932).

[442d] J. Zawadsky and Bretsznajder, *Z. physik. Chem.*, B **22**, 60, 79 (1933).

CHAPTER XIX

MICRO-HETEROGENEOUS AND BIO-CATALYSIS

THERE still remains for brief consideration a form of catalysis which, in a certain sense, stands midway between homogeneous and heterogeneous catalysis, namely catalysis by colloidal or micro-heterogeneous catalysts. It is principally a question of catalysis in solutions, consequent upon the nature or the state of division of colloidal materials. To this class belong, on the one hand, catalyses by colloidal metals and, on the other hand, those processes effected by organic colloids, the ferments or enzymes, which are the catalysts for chemical changes in the living organism.

Both fields have undergone a degree of expansion such that each has grown, and especially in the latter case, to a special branch of science. The intensive study of enzymes by Willstätter and his school is particularly responsible for this. It will not, therefore, be possible for us, within the space available, to consider these phenomena in the same detail as that obtaining in the earlier sections. There are on this subject many monographs of both large and small compass from the ablest of authors to which reference may be made.[443, 444, 445, 446, 447, 448] Concerning colloidal metals reference may be made to the works of Hückel [449] and Bredig.[450] We shall, therefore, limit ourselves to a discussion of both fields from the standpoint of analogies between the two and between each of them and the forms of catalysis already discussed.[450a]

Preparation of Colloidal Metals: The preparation of colloidal metals can be carried out in two ways. Either one may disperse the metals under

[443] R. Willstätter, Untersuchungen über Enzyme, Berlin, 1928.

[444] J. Oppenheimer and R. Kuhn, Die Fermente und ihre Wirkungen, Leipzig, 1925.

[445] E. Waldschmidt-Leitz, Die Enzyme, Braunschweig, 1926.

[446] W. Grassmann, Neue Methode und Ergebnisse der Enzymforschung, Munich, 1928.

[447] H. von Euler, Bio-Catalysts, Ahrens Sammlung, Stuttgart, 1930.

[448] O. Warburg, Katalytische Wirkung der lebenden Substanz, Berlin, 1928.

[449] W. Hückel, Katalyse mit kolloiden Metallen, Leipzig, 1927.

[450] G. Bredig, Alexander's Colloid Chemistry, Vol. 2, pp. 329 ff. *Chem. Catalog Co.*, New York, 1928.

[450a] See W. Frankenburger, *Ergebn. d. Enzymforschung* 3, 1 (1934) for a discussion of the topics last mentioned.

water in an electric arc between electrodes of the metal in question, as was done by Bredig,[450] or in organic media using oscillatory currents, in the manner devised by Svedberg.[451] Nickel, for technical hydrogenation, is prepared by reduction, with hydrogen, of nickel compounds at moderate temperatures in the liquid medium itself. In this way the metal is obtained without admixtures, a circumstance which is especially desirable in reaction-kinetic studies of activity.[450]

The other method, of especial use in the preparation of stable hydrogenation catalysts for preparative purposes, depends upon the application of protective colloids. These permit the catalyst to be employed in higher concentrations in that they prevent agglomeration. The protective colloids therefore exert a kind of structural promotion (pp. 300, 303). Compounds of the respective metals, mainly platinum, iridium and palladium, are reduced in solution in the presence of protective colloids. Protalbinic and lysalbinic acids are used in the method of Paal; gum arabic or gelatine is used in the Skita method.[449]

Conditions are not so simple in the case of colloidal organic catalysts, the enzymes. We are still quite uncertain as to their material nature. Although they were included by Berzelius in his definition of catalysis, it has only been known since the time of Buchner [452] that they are also active outside the living cell, and are, therefore, catalytic substances. On the other hand, their chemical nature is still unknown to us because we have not succeeded in isolating the enzymes, that is to say, in separating them completely from the materials with which they are associated, with which they are present in nature. Nevertheless, we know that such a separation must, in principle, be possible. Willstätter has shown the path in this direction and traveled far along that path. He makes use of the selective adsorbability of the enzymes as compared with their associated materials on acid (silica) or basic (alumina) adsorbents. The experimental ingenuity of Willstätter and his co-workers has permitted, for example, the separation from pancreas of a fat-splitting lipase, a starch-splitting amylase, the protein-splitting trypsin and the peptide-splitting erepsin. They have succeeded in transplanting the active group from one adsorbent to another without loss.

Nevertheless it has not yet been possible by these methods so far to purify enzymes from the associated substances that any assumptions regarding their chemical nature can be made. But, by following the increase in

[451] T. Svedberg, Methoden zur Herstellung kolloider Lösungen, Dresden and Leipzig, 1923.

[452] H. Buchner, *Ber.*, 30, 117 (1897).

activity due to continued processes of purification, the probability that enzymes are chemical individuals has been materially increased. Further, that they are colloids is directly demonstrable with the preparations obtained. Whether this must be so in principle is uncertain but also probable. Willstätter [10] considers an enzyme as a specific active atomic grouping on a colloidal carrier.

Kinetics: The kinetics of micro-heterogeneous catalysis are determined by the colloidal state. Bredig and Teletow [453] have compared the kinetics of hydrogen peroxide decomposition at platinized platinum surfaces with those at the surface of colloidal platinum. In the first case, owing to the small velocity of diffusion through the aqueous solution, we have a case of the type discussed on page 221, in which the reaction velocity is large compared with the velocity of diffusion of the substrate and so the latter is measured. A first order reaction is observed with a quite small temperature coefficient. The velocity of stirring of the solution has a great influence on the velocity since it determines the thickness of the adhering diffusion layer.

Conditions are quite different in the case of micro-heterogeneous catalysis. Actually the process measured is in this case, also, first order both with platinum and with the peroxide-splitting enzyme, catalase.

TABLE XXXVIII
HYDROGEN PEROXIDE DECOMPOSITION BY CATALASE AND PLATINUM SOL

Blood Catalase (Senter)			Platinum Sol (Bredig and Muller von Berneck)		
Time	H_2O_2	k	Time	H_2O_2	k
0	39.7	—	0	47.4	—
5	32.2	0.0175	10	37.9	0.0097
10	26.7	0.0163	20	30.0	0.0099
20	17.8	0.0178	30	23 6	0.0101
30	11.6	0.0185	40	18 2	0.0104
50	4.8	0 0191	60	11.0	0.0106

However, the temperature coefficient is markedly higher, and is of the order of that of chemical reactions. It is also understandable that colloid particles with their rapid Brownian motion are not surrounded in the same manner as bulk material by a constant diffusion layer. As a consequence, the velocity of stirring is, in this case, without influence.

[453] G. Bredig and J. Teletow, *Z. Elektrochem.*, 12, 581 (1906).

If we turn to alkaline solutions, the macro-heterogeneous catalysis is scarcely influenced whereas the colloidal catalysis even changes its order of reaction. It now becomes of zero order; we already know (page 223) that this implies a rate-determining reaction in the surface of the submicrons completely saturated with substrate. Also, hydrogenation reactions at colloidal metal surfaces are of zero order, occur therefore at surfaces saturated with substrate. Further data on such processes, as well as several anomalies are discussed by W. Hückel.[449] In the preceding tables we see some evidence of a change to this state of affairs. The first order constants rise somewhat with increased conversion. This implies merely that the reaction is taking place according to the well-known equation for reaction in a layer showing moderate adsorption (page 223),

$$\frac{dx}{dt} = \frac{kp}{1 + bp},$$

where p in this case refers to the concentration of substrate.

A kinetics of this form is found quite definitely for very many enzyme reactions especially in the inversion of cane sugar by saccharase from yeast and above all in the hydrolysis of esters by esterases.

It is of interest to note that this equation can be derived without regard to the micro-heterogeneous nature of this catalysis for the special case of enzyme reactions, by Henri [454] and especially by Michaelis and Menten,[455] using a quite different method involving intermediate compounds in homogeneous phase.

The following processes are assumed:

$$(1)\ \mathrm{E} + \mathrm{AB} \xrightarrow{k_1} \mathrm{EAB}$$

$$(2)\ \mathrm{EAB} \xrightarrow{k_2} \mathrm{E} + \mathrm{AB}$$

$$(3)\ \mathrm{EAB} \xrightarrow{k_3} \mathrm{E} + \mathrm{A} + \mathrm{B}.$$

If the symbols in brackets denote concentrations of substances, [E] the total concentration of enzyme used, [AB] the concentration of cane sugar and [EAB] that of the intermediate compound, cane sugar-enzyme, which determines reaction, to be thought of as an Arrhenius intermediate, then,

[454] V. Henri, *Helv. Chim. Acta*, **39**, 194 (1902).

[455] L. Michaelis and M. L. Menten, *Biochem. Z.*, **49**, 333 (1913).

according to the mass action law,

$$\frac{[AB]\,([E]-[EAB])}{[EAB]} = \frac{k_2}{k_1}$$

or

$$[EAB] = \frac{[AB]\,[E]}{[AB] + k_2/k_1}.$$

If the decomposition into E, A and B be assumed unimolecular, the concentration of the water used in the hydrolysis remaining sensibly constant, the following equations obtain

$$\frac{dx}{dt} = k_3\,[EAB] = \frac{k_3[AB]\,[E]}{[AB] + k_2/k_1} = \frac{k_3 \cdot k_1/k_2[AB]}{1 + k_1/k_2[AB]}\,[E].$$

It will be seen that this last expression is identical with that obtained for an adsorption of a substrate of concentration [AB] at a surface [E]. The analogy is naturally more than a formal one; in place of the available surface there enters the amount of available enzyme. In place of the surface occupied, σ, there is the concentration [EAB] or, more correctly, [EAB]/[E]. In place of the adsorption coefficient, b, we find the equilibrium constant, k_1/k_2. In both methods of presentation it is the adsorption complex or compound of catalyst and substrate, an Arrhenius intermediate, that we must primarily keep in mind. It will be remembered that we have already derived this special case in the consideration of homogeneous catalysis as developed by Spitalsky (p. 75).

It will thus be seen that the analogy between enzyme kinetics and heterogeneous catalysis does not prove that the former is actually a case of micro-heterogeneous catalysis. Among others, Hitchcock,[456] Schwab,[257] and more recently Weidenhagen [457] have emphasized this. On the other hand, the enzymes, together with the colloidal metals, form the connecting link between homogeneous and heterogeneous catalysis. If it should once happen, as is quite possible in principle, that the active groups of an enzyme could be separated from the carrier-residues and studied in homogeneous solution, this would in no way alter the kinetics, as has already been shown; we could regard such a homogeneous enzyme as a contact agent whose active centers are set free.

With respect also to the inhibition due to reaction products, heterogeneous and enzyme kinetics are entirely analogous; for the retardation of sugar inversion by glucose or fructose, we obtain, with Michaelis and Menten, the same equations that have been found applicable to retarded hetero-

[456] D. J. Hitchcock, *J. Am. Chem. Soc.*, **48**, 2870 (1926).

[457] R. Weidenhagen, Laudt and F. Todt, *Z. Ver. deut. Zuckerind.*, **80**, 25, 81 (1930).

geneous reactions. If we add to the above scheme the following reactions:

$$(4)\ \mathrm{E} + \mathrm{B} \xrightarrow{k_4} \mathrm{EB}$$

and

$$(5)\ \mathrm{EB} \xrightarrow{k_5} \mathrm{E} + \mathrm{B},$$

we obtain the kinetic expression,

$$\frac{dx}{dt} = \frac{k_3 k_1/k_2\,[\mathrm{AB}]}{1 + k_1/k_2[\mathrm{AB}] + k_4/k_5[\mathrm{B}]}[\mathrm{E}].$$

Quite recently, W. Langenbeck [458] has proposed a quite different presentation of enzyme kinetics. He starts from experience with organic molecules as ferment-models, in which the activity depends on an intermediate compound with only one part of the substrate; an activity, moreover, which, by suitable substitution, in analogy with the case of enzyme carriers, can be considerably enhanced. He formulates the corresponding processes in the following manner:

$$(1)\ \mathrm{E} + \mathrm{AB} \xrightarrow{k_1} \mathrm{EA} + \mathrm{B}$$

$$(2)\ \mathrm{B} + \mathrm{EA} \xrightarrow{k_2} \mathrm{E} + \mathrm{AB}$$

$$(3)\ \mathrm{EA} \xrightarrow{k_3} \mathrm{E} + \mathrm{A},$$

and obtains, without assuming an Arrhenius character for the intermediate, the following final equation:

$$\frac{dx}{dt} = \frac{k_1[\mathrm{AB}]}{1 + k_1/k_3[\mathrm{AB}] + k_2/k_3[\mathrm{B}]}[\mathrm{E}].$$

This expression is identical with that derived by Michaelis and Menten but the constants have a different significance. Such equations, therefore, cannot decide between two mechanisms. They differ in one important point. In the older formulation an enzyme-substrate compound is first formed, which then decomposes, the substrate breaking into fragments. Retardation by reaction products, if present, consists therefore in a competition for the enzyme. In the newer formulation, the substrate splits in the process of formation of the enzyme compound and the retardation consists in a reversal of this process. Langenbeck himself sees also a distinction in that his theory envisages a catalysis involving principal valences, while the older theory involves secondary valences. Nevertheless, as Schwab

[458] W. Langenbeck, *Ergebn. d. Enzymforsch.*, **2**, 314 (1933); *Ergebn. d. Physiol. u. Exp. Pharm.*, **35**, 470 (1933); *Z. Elektrochem.*, **40**, 485 (1934).

has pointed out,[459] the catalytically active adsorption forces are to be reckoned likewise as true homopolar valences.

It now seems that, as in an earlier case (page 73), experiments with the heavy hydrogen isotopes can bring about a decision between the alternatives. First, we may set forth, in parallel columns, to what formulations both theories lead in different special circumstances:

A. No Retardation

Michaelis-Menten	Langenbeck
$\frac{k_4}{k_5}[\mathrm{B}] \ll \frac{k_1}{k_2}[\mathrm{AB}]$	$k_2[\mathrm{B}] \ll k_3$
$\frac{dx}{dt} = \frac{(k_1k_3/k_2)\,[\mathrm{AB}]\,[\mathrm{E}]}{1 + (k_1/k_2)\,[\mathrm{AB}]}$	$\frac{dx}{dt} = \frac{k_1\,[\mathrm{AB}]\,[\mathrm{E}]}{1 + (k_1/k_3)\,[\mathrm{AB}]}$

From these, the following limiting cases may be derived:

B. Zero order

Michaelis-Menten	Langenbeck
$k_1\,[\mathrm{AB}] \gg k_2$	$k_1\,[\mathrm{AB}] \gg k_3$
(Saturation Adsorption)	(Arrhenius Intermediate)
$\frac{dx}{dt} = k_3[\mathrm{E}]$	$\frac{dx}{dt} = k_3[\mathrm{E}]$

C. First Order

Michaelis-Menten	Langenbeck
$k_2 \gg k_1[\mathrm{AB}]$	$k_3 \gg k_1[\mathrm{AB}]$
(Weak Adsorption)	(van't Hoff Intermediate)
$\frac{dx}{dt} = (k_1k_3/k_2)\,[\mathrm{AB}]\,[\mathrm{E}]$	$\frac{dx}{dt} = k_1[\mathrm{AB}]\,[\mathrm{E}]$

For high substrate concentrations (Case B) both theories indicate that the measured constant of zero order is a velocity constant. Such constants are quite generally smaller in heavy water compared with those in light water. Actually, Bonhoeffer and Salzer [460] find that the hydrolyses of numerous glucosides by emulsin are retarded by heavy water with saturation of the enzyme by the substrate.

[459] G.-M. Schwab, *Z. Elektrochem.*, **40**, 487 (1934).

[460] K. F. Bonhoeffer and Salzer, *Z. physik. Chem.*, A **175**, 304 (1936); *Naturwiss.*, **23**, 867 (1935).

For lower substrate concentrations and first order processes (Case C), however, the measured velocity according to Michaelis and Menten is the product of the velocity constant k_3 and the equilibrium constant k_1/k_2; according to Langenbeck, on the contrary, it is simply the velocity constant k_1 of the primary step. According to the latter, therefore, we might expect, under any circumstances, a retardation by heavy water. Actually, in the hydrolysis of the methyl glucoside, where a first order reaction prevails, an *acceleration* was found. This is understandable, on the Michaelis-Menten theory, as due to a higher enzyme-substrate affinity in heavy water. Bonhoeffer and Salzer conclude therefore that, in the hydrolytic enzyme processes, the occurrence of an Arrhenius enzyme-substrate intermediate is proved. Similar conclusions were reached in the case of catalysis by hydrogen ions (p. 73).

There exists, however, a second form of retardation, for example, by glycerine which does not depend on a displacement of the substrate from the enzyme but affects the velocity of decomposition, k, of the compound. It is difficult, thus far, to interpret this with certainty.

One further agreement connects enzyme reactions, not so much with heterogeneous catalysis, but very closely with micro-heterogeneous catalysis, and that is the dependence of the activity of the catalysts on the hydrogen ion concentration of the medium. With colloidal metals as also with enzymes, in precisely the same form it is found that the reaction velocity passes through a maximum at a definite p_H value. An explanation of this has been sought, particularly by Michaelis, in the assumption that sometimes the anion or only the cation or in other cases the neutral part, or zwitterion, is catalytically active. This explanation does not indeed cover all the factors of importance that enter into the question, first, because it can often only explain a one-sided rise with p_H; above all, however, because the affinity constant K does not change with p_H. This latter fact would suggest an effect on the k, that is, on the decomposition of the intermediate compound; while the fact that the position of the maximum often changes with the substrate indicates that its electrolyte nature is a determining factor. For the case of colloidal metals one can indeed make similar assumptions, for example, the surface formation of intermediate hydroxides at definite p_H values. That, also in this case, the dissociation of the substrate is a determining factor, has already been learned from the discussion of the catalysis of hydrogen peroxide by silver (page 258) in which the acid nature of the peroxide determines the optimum velocity. In the case of enzymes there is the additional possibility that the accompanying substances which determine the colloidal behavior also determine

the optimum, with the result that the maximum changes its position with further purification (page 77).

Poisoning: Catalysts of high dispersion, both inorganic and organic, are also liable to poisoning by even minute amounts of foreign substances. It is worthy of note that often the same poisons affect, for example, both platinum sol and organic catalases. Hydrogen sulphide, hydrogen cyanide, and mercuric chloride are prominent examples. Nevertheless, here again, different catalysts have different sensitivities for the same poison. While blood catalase is strongly poisoned by hydrogen cyanide the reverse is the case with the protein-splitting enzymes such as trypsin and pepsin. On the other hand, there do not appear to be cases among enzymes, in which, as is frequently the case in heterogeneous catalysis, a catalyst is poisoned for only a part of its reactions. This is actually an indication that the preparations now available are more homogeneous in their active constituent that synthetic catalysts.

Promoter Action: It is especially characteristic of enzymes that they show a behavior which is reminiscent of promoter action in inorganic mixed catalysts. Willstätter [10] has emphasized the similarity which obtains in this respect between the catalytic reactions of living matter and those of chemical industry. Analogous phenomena with colloidal metals are scarcely known unless we include, with Bredig,[450] the case of hydrogen peroxide decomposition accelerated at silver surfaces by hydroxyl ions (page 258).

The most frequent cases are promotions due to " activators " or " co-enzymes " in the protein-splitting plant and animal " proteases." The same substances which act as strong poisons to the catalases, especially hydrogen sulphide and hydrogen cyanide, act as promoters towards the protease, pepsin. Conditions are especially interesting in the case of trypsin, an albumen-splitting ferment of the pancreas. Prepared in pure form it is only active with a restricted number of proteins. In the intestine, however, it is promoted by a co-enzyme there present, enterokinase, so that it now can rapidly split even the higher albumens such as albumin and fibrin. Examples of this kind in which, analogous to the technical contact catalysts, the activity of the enzyme is increased or its specificity or selectivity altered might be multiplied. Examples or three-component catalysts are also known.

The explanations that are given for such phenomena are entirely analogous to those discussed under heterogeneous mixed catalysts. Enzymic phenomena have indeed contributed much to the concept of synergy. In these cases also, it is assumed that, by adsorption, or, what is the same thing, by chemical compound formation between the mixed components, at the

points of contact, centers are produced of especial valence activity at which the substrate is more strongly bound and more active than at the enzyme only. In particular, the theory of Euler,[447] according to which the two fragments of the substrate about to be formed must be bound through two different modes of binding (in the sense of a doublet or multiplet theory of adsorption, page 305), leads one to expect such promoter effects in two component systems.

Selectivity: Selectivity in micro-heterogeneous systems is especially marked. For different groups of reactions the organism employs different catalysts just as does industry. Thus, in plants and animals, there are esterases which only hydrolyze esters, proteases which digest albumens, and among these again there is a selectivity determined by the structural position of the group $-HN-CO-$ to be hydrolyzed; aminoacylases which split amino-acids, carbohydrases which hydrolyze carbohydrates such as polysaccharides and glucosides, oxidases which oxidize and dehydrogenases which transfer hydrogen, catalases which split peroxides and the fermentation enzymes. The classification is naturally arbitrary and can be made more definite or comprehensive at various points. The enzymes are optically specific, which is to be associated with the presence of only one active form of substances in the organism. How this specificity can be interpreted quantitatively with the aid of the Michaelis-Menten theory through differences of reaction velocities and equilibria has recently been demonstrated by Schwab, Bamann and Laeverenz.[461] It is noteworthy that, in this case, as in others, not only complexes of the form EAB but also complexes of the form $E(AB)_2$ must be assumed.

Quite a number of these enzymic functions can now be imitated by colloidal metals or 'inorganic ferments' (Bredig). We are already familiar with their behavior as catalases, as dehydrogenases and, also, in the reverse direction as hydrogenation catalysts for organic substances, many metals are active. Formaldehyde and formic acid are good examples of substances dehydrogenated by the noble metals,

$$CH_2O = CO + H_2$$
$$HCOOH = CO_2 + H_2.$$

The first reaction, in the presence of methylene blue as acceptor for the hydrogen produced, that is to say, the reduction of this dye by formaldehyde, is also effected by a ferment present in milk. The reaction is known as Schardinger's reaction. A model of this reaction is also available in the form of colloidal platinum. For enzyme models, which imitate the optical

[461] G.-M. Schwab, Bamann and Laeverenz, *Z. physiolog. Chem.*, **215**, 121 (1933).

specificity of natural ferments, as constructed by Bredig and Schwab, see page 341.

The arrangement of all these catalytic enzyme actions in the progression of living processes is, at the present time, the principal problem of physiological chemistry, since, in all organisms important in the life process, specific enzymes are found. Hence, it must be assumed that the chemical processes of life are essentially catalytic processes. Whilst the hydrolytic reactions which have been discussed serve to break down the food, which is imbibed, into simpler structural units or to build from these latter actual bodily material, the processes of oxidation and reduction, hydrogenation and dehydrogenation are simultaneously occurring as agencies for the production of energy for the mechanical and endothermic chemical reactions of the living organism.

On the one hand we are concerned with the taking of molecular oxygen from the air, with respiration in its widest sense. Warburg has demonstrated the activity of special respiratory ferments, in animal organisms the haemin-type substances containing iron. These may also be imitated in inorganic examples by means of iron promoted charcoal preparations. The model, like the original, is poisoned in its oxidation activity by the same typical respiratory poisons such as hydrogen cyanide and narcotics. These latter evidently enter into combination in both cases with the active iron centers and so, by displacement, prevent their valences from adsorbing the organic substrate to be oxidized.

On the other hand, the catalysts which bring about the reverse process of assimilation in plants play an analogous rôle. For example, in the case of chlorophyll, they make light energy available for this endothermic process, in that they act partly as photosensitizers and partly as adsorption catalysts making the molecule adsorbed more reactive. The process consists in the first place of an activation of molecular oxygen by a respiratory ferment and transfer to the hydrogen of a second intermediate, which in its turn receives hydrogen from a third so that, in a complete enzyme chain, hydrogen is always made available and activated by hydrogenases and dehydrogenases.

A modern contribution to the mechanism of enzyme reactions which involves the removal of one hydrogen atom from a substrate by the catalyst and the subsequent interaction of the resultant radical with oxygen by a chain mechanism in the body of the substrate was recently put forward by Haber and Willstätter [462] and applied also to various other types of enzyme reaction.

[462] F. Haber and R. Willstätter, *Ber.*, **64**, 2844 (1931).

The same uncertainty as to precise mechanism applies quite generally to the further processes which determine the fate of oxidation or dehydrogenation products in their passage from the blood into their appropriate organs. In particular, the muscle plays an important rôle, working at the expense of the oxidation or dehydrogenation potentials provided by the respiratory process. The mechanism is not yet explained, but in any case the energy is consumed simultaneously with the formation of tissue and degradation products, through a whole series of intermediate stages of successive degrees of dehydrogenation which all pass one into another by means of specific dehydrogenases. Among them glutathione, for example, seems to play a part in that, in its disulphide form, it binds hydrogen-donors, takes hydrogen from them (see the quantum-mechanical opening-up of the substrate by attachment to the catalyst, pp. 243, 248) and goes over as a result into the hydrosulphide form which then transfers the hydrogen to the hydrogen-acceptor attached to it. This is only given as one example of mechanism.

What has here been given from the very extensive field of knowledge of physiological chemistry, naturally quite general in character and illustrative only in its nature, should serve but to show that there is in it a quite extensive field for the application of micro-heterogeneous catalysis and of catalysis that, in addition, is of the greatest fundamental significance.

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